

STANDARDS DEVELOPMENT BRANCH OMCE



36936000004272

LEACHING STUDIES OF POLYCHLORINATED DIBENZODIOXINS AND POLY-
CHLORINATED DIBENZOFURANS FROM MUNICIPAL INCINERATOR FLYASH

Final Report of Project 126 RR

TD
797
.K36
1987
MOE

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact ServiceOntario Publications at copyright@ontario.ca

**TD
797
.K36
1987**

Leaching studies of
polychlorinated dibenzodioxins
and polychlorinated
dibenzofurans from municipal
76637

LEACHING STUDIES OF POLYCHLORINATED DIBENZODIOXINS AND POLY-
CHLORINATED DIBENZOFURANS FROM MUNICIPAL INCINERATOR FLYASH

Final Report of Project 126 RR

To: Ontario Ministry of the Environment

Submitted by: F.W. Karasek

H.Y. Tong

G.J. Reuel

Chemistry Department,

University of Waterloo,

Waterloo, Ontario. N2L 3G1

DISCLAIMER

"This report has been reviewed by the Research Advisory Committee of the Ministry of the Environment and approved for publication. Approval does not necessarily signify that the contents reflect the views and/or policies of the Ontario Ministry of the Environment nor does mention of trade names or commercial products constitute endorsement or recommendation for use".

© 1987 Her Majesty the Queen in Right of Ontario
as represented by the Minister of Environment

SUMMARY

This study concerns the possibility of polychlorodibenzo-p-dioxins (PCDD), polychlorodibenzofurans (PCDF) and other organic compounds entering the environment through the leaching of municipal incinerator flyash into water. The study also takes into account the effect of the pH of water on the extent of leaching.

To simulate the conditions by which flyash comes into contact with water several methods were investigated. A Soxhlet extraction of flyash using water was finally chosen for this leaching study because of its simulation of the circulation of water in nature and because of its efficient use of a small volume of water. Following the extraction, a simple benzene-water partitioning step was used to transfer the organic compounds in the water extracts into organic solvent for a subsequent GC and GC/MS analysis. Good recovery of PCDD at the 2 ppt level was obtained using benzene partitioning.

The analytical results for water extracts at pH levels of 4, 7, and 10 show that PCDD and PCDF enter water through leaching. These compounds were found in water at the 1 to 400 ppt level and are at very low concentration compared to the amount of PCDD and PCDF typically found in this flyash. Because of these low concentration levels the reproducibility and accurate quantitative results were poor. The results indicate that PCDD and PCDF are very strongly bound to the flyash. The rate of leaching in nature from rain and ground water is very slow compared to the leaching occurring in a Soxhlet extractor and it is doubtful whether any PCDD or PCDF will enter the water system. The extractability using this method may actually represent many months, or perhaps years, of leaching. It is also important to note that the most toxic congeners (tetra) were found at the lowest concentration.

The study was extended to identification of other organic compounds that were also leached from the flyash into the water extracts. Identification of these organic compounds was accomplished using the techniques of GC/FID, GC/EIMS,

GC/PICIMS and GC/NICIMS. These compounds were present at higher concentrations than the PCDD and PCDF and many were chlorinated. At pH 4, a total of 71 compounds were found; at pH 7, 64 were found, and at pH 10, 56.

The extraction procedure described in this report, provides a quick and easy method for the determination of the extent of potential leaching from samples such as flyash. The method does not take into account factors such as soil attenuation and temperature but it does provide a means of evaluating leaching under the worst conditions possible.

SOMMAIRE

La présente étude porte sur la possibilité que les polychlorodibenzo paradioxines (PCDD), les polychlorodibenzofurannes (PCDF) et d'autres composés organiques polluent l'environnement par la lixiviation dans l'eau des cendres volantes qui proviennent d'incinérateurs municipaux. L'étude s'intéresse également à l'effet du pH de l'eau sur l'importance de la lixiviation.

Afin de simuler les conditions dans lesquelles les cendres volantes entrent en contact avec l'eau, plusieurs méthodes ont été étudiées. L'extraction par l'eau des composés des cendres volantes à l'aide d'un soxhlet a été choisie pour la présente étude de lixiviation parce qu'elle permet de simuler la circulation de l'eau en milieu naturel et d'utiliser efficacement un faible volume d'eau. Après l'extraction, une simple séparation benzène-eau a été effectuée afin de transférer les composés organiques présents dans les échantillons d'eau dans un solvant organique pour analyse ultérieure par GC et GC/MS. Par la séparation au benzène, une bonne récupération des PCDD a été effectuée à une concentration de 2 o/oo.

Les résultats de l'analyse d'échantillons d'eau de pH 4, 7 et 10 démontrent que les PCDD et que les PCDF contaminent l'eau par lixiviation. Ces composés ont été trouvés dans l'eau à une concentration de 1 à 400 o/oo, ce qui est très faible par comparaison à la quantité de PCDD et de PCDF que l'on trouve habituellement dans les cendres volantes. En raison de ces faibles concentrations, la reproductibilité et la précision des mesures quantitatives ont été médiocres. Les résultats indiquent que les PCDD et les PCDF sont très fortement liés aux cendres volantes. Le taux de lixiviation en milieu naturel par la pluie et les eaux souterraines est très faible par comparaison à la lixiviation qui se produit dans un extracteur soxhlet, et on doute que des PCDD ou des PCDF puissent s'infiltrer dans le réseau hydrographique. La capacité d'extraction de cette méthode peut en fait représenter de nombreux mois, voire même des années

de lixiviation. Il est également important de noter que les congénères (tétra) les plus toxiques étaient ceux dont la concentration était la plus faible.

L'étude a également permis de déceler, au moyen des techniques de GC/FID, de GC/EIMS, de GC/PICIMS et de GC/NICIMS, d'autres composés organiques qui passent des cendres volantes aux échantillons d'eau par lixiviation. Ces composés étaient présents à des concentrations plus élevées que les PCDD et les PCDF, et beaucoup étaient chlorés. Au pH 4, un total de 71 composés ont été découverts; au pH 7, 64 et au pH 10, 56.

La procédure d'extraction décrite dans le présent rapport constitue une méthode facile et rapide pour déterminer l'ampleur de la lixiviation possible à partir de substances telles que les cendres volantes. Cette méthode ne tient pas compte de facteurs tels que l'effet tampon du sol et la température, mais elle permet d'évaluer la lixiviation dans les conditions les plus défavorables.

INTRODUCTION

In many large cities throughout the world, municipal waste is disposed of by incineration in large plants. The amount of urban waste disposed of in this manner worldwide is large. Canada, for example, disposes of an estimated 2.0 million tons of waste by incineration annually. A fine particulate known as flyash is formed in the combustion zone in the incinerator. This product is precipitated electrostatically and then requires disposal. Approximately 35,000 tons of flyash are produced for each million tons of waste incinerated. It is therefore important to study the environmental and health effects of flyash.

The composition of flyash has been studied extensively. It is composed of 70-95% inorganic matter such as SiO_2 , Al_2O_3 , Na_2O , and Fe_2O_3 (1). Adsorbed on the inorganic matter are many organic compounds in the parts-per-million to parts-per-billion range. More than 600 organic compounds are known to be present, 200 of which have been identified in this complex organic mixture. These compounds include hydrocarbons, phthalates, polycyclic aromatic hydrocarbons (PAH) and polychlorinated organic compounds (2).

Some of the organic compounds identified in flyash are known to be toxic. Some PAH found in flyash are toxic, carcinogenic and mutagenic (3). Of special concern are two classes of compounds known as polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). These two compound classes are formed by chlorine atom substitution on the dibenzo-p-dioxin and dibenzofuran respectively. Because of the different numbers of chlorine atoms and the different substitution patterns possible, 75 PCDD and 135 PCDF congeners exist, most of which are known to be present in flyash. Some PCDD congeners, especially 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) are extremely toxic (4). Recently, public concern about the toxicity of the PCDF has been growing. Because these hazardous compounds are found in municipal flyash, regardless of the design of the incinerator or the type of garbage burned, the effect of flyash residue in the

environment is an important issue.

One way in which flyash enters the environment is through stack emission. Approximately 1-2% of the flyash produced is not captured by the electrostatic precipitators and escapes to the atmosphere with the stack gases (4). This visible, airborne emission is generally the aspect of flyash pollution found most objectionable by urban centres.

Most of the flyash, however, is trapped by the precipitators and has to be disposed of in some manner. Flyash is most often dumped or buried in landfill sites. This method of disposal seems the most economical and practical. However, the flyash buried in a landfill site is constantly exposed to ground water, which presents the possibility of leaching toxic organic compounds. The flyash is exposed to rain-water and possibly to waste-water as well. It is important to know whether PCDD and PCDF or other organic pollutants in the flyash could be removed by water leaching and contaminate the environment. Little investigation has been done regarding this possibility.

The major purpose of this study was to investigate the possibility of PCDD and PCDF entering the environment through the leaching of flyash with water. The behaviour of other organic compounds in flyash was also investigated. The most important step in the study was to design an experiment that would resemble actual conditions in which flyash comes into contact with water. Several difficulties were foreseen in the design of the experiment. First, water is not a good solvent for organic compounds. Therefore, assuming that organic compounds would indeed leach from the flyash, a large volume of water would be needed to leach sufficient organic material for a chemical analysis. Second, the strong tendency for PCDD and PCDF to adsorb onto glass necessitates that the aqueous organic mixture be exposed to a minimal surface area of glass.

The general method chosen to represent the leaching process was extraction of organic compounds from flyash with water. An exhaustive extraction, provides an

estimate of the extent of leaching in the most serious case, where the flyash is in a totally aqueous environment.

Manual and ultrasonic agitation of flyash were tried and were found to have low extraction efficiencies. Accelerated leaching was obtained using a Soxhlet apparatus. The basic process of a Soxhlet extraction is very similar to the natural circulation of water - vapourization, condensation, and precipitation. The Soxhlet extraction, therefore, seemed most representative of the actual leaching process in disposal sites. In addition, fresh solvent is passed through the flyash during each cycle, thereby achieving efficient use of a small volume of water.

To expose the organic compounds in the water extract to a minimal glass surface area, benzene-water partitioning following the Soxhlet extraction was used to transfer the organic compounds in the water extract to benzene for the subsequent analysis.

Because of exposure to different water sources which include industrial wastewater, flyash in landfill could be exposed to water with different pH conditions. Another aim of this project was to study the effect of pH of the water on leaching of flyash. Three pH values were used: 4, 7 and 10. Those three pH values cover the normal pH range of waste water discharged from most industries. An acid and a base were successfully used to ensure proper pH conditions in the thimble of the extractor. The organic compounds in the water extracts obtained from the three different conditions were subjected to an extensive analysis.

In this report, the different methods used for the extraction are described. The methods used for pH adjustment in Soxhlet extraction are also demonstrated. However, the discussions are focused on the results obtained from the Soxhlet extraction since it is most representative of the leaching of organic compounds from flyash into water. Five techniques were used in the course of analysis of PCDD, PCDF and other organic compounds in the water extracts of flyash. They included gas chromatography with flame ionization detection (GC/FID) and with

electron capture detection (GC/ECD), gas chromatography/mass spectrometry with electron impact ionization (GC/EIMS), with positive ion chemical ionization (GC/PICIMS), and with negative ion chemical ionization (GC/NICIMS). PCDD, PCDF and a number of other organic compounds were found in the water extracts of flyash by these analytical methods. A comparison of the other organic compounds found in different water extracts is presented.

In order to determine how well dioxins that leach into the water can be detected, a recovery study using dioxin standards was also performed. This study gave good recovery of dioxins at a 2 ppt level in water based on GC/ECD analysis.

EXPERIMENTAL

Solvents and Standards

All solvents used were distilled in glass, UV grade, supplied by Caledon Laboratories (Georgetown, Ontario, Canada), with the exception of the water, which was deionized tap water. The standards of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1234-TCDD), 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (123478-H₆CDD), 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin (1234678-H₇CDD) and octachlorodibenzo-p-dioxin (OCDD) were all purchased from Ultra Scientific (Hope, RI, USA). The standard of 1,2,3,4,7-pentachlorodibenzo-p-dioxin (12347-P₅CDD) was obtained from Cambridge Isotope Laboratories Inc. (Woburn, MA). The formic acid, sulfuric acid and sodium hydroxide were purchased from J.T. Baker Chemical Co. (Phillipsburg, NJ, USA) and the 2-methoxyethylamine was purchased from Aldrich Chemical Co. (Milwaukee, Wis., USA). All glassware was cleaned by ultrasonic agitation in water and detergent powder (Canadian Laboratory Supplies) for 30 min. The glassware was rinsed with copious amounts of tap water followed by deionized water, prior to drying at 250°C for 3 hrs. The glassware was rinsed three times with benzene, 3 times with dichloromethane, and allowed to air dry completely immediately before use.

Sample Collection

The flyash sample was collected in kilogram amounts by grab sampling from the electrostatic precipitator of a municipal incinerator in Toronto, Ontario, Canada. The sample was stored at room temperature, away from ultraviolet and visible light.

Extraction of Flyash with Water

(a) Manual Agitation

A round bottom flask containing 50 g flyash and 250 mL water was capped with a glass stopper, shaken briskly for 30 sec and allowed to settle for 30

min. The supernatant was decanted into a separatory funnel through a glass wool plug and solvent extracted with 3 X 100 mL aliquots of benzene, which were collected in a round bottom flask and concentrated to approximately 15 mL by rotary evaporation under aspirator vacuum. This extract was transferred to a cone bottom flask, along with several benzene rinses of the round bottom flask, and the volume of benzene was further reduced in the same manner to approximately 5 mL. The organic phase (upper) was transferred by Pasteur pipet to a small pear shape flask along with several benzene rinses of the cone bottom flask, being careful not to transfer any of the aqueous phase (lower). The volume of the organic extract was reduced by rotary evaporation to approximately 5 mL and transferred to a calibrated 1 mL reacti-vial. The volume of the extract was reduced to 50 μ L under a gentle stream of high purity nitrogen. The reacti-vial was sealed with a screw cap fitted with a Teflon-faced liner and stored at -15°C for the subsequent analysis. This procedure was performed in duplicate.

(b) Manual and Ultrasonic Agitation

The same method as described above was used with the following exceptions. After the hand agitation, the contents of the flask were mixed using ultrasonic agitation for 10 min. The contents of the flask were allowed to settle for 1 hr. After the supernatant was decanted, a fresh 250 mL volume of water was added to the round bottom flask and the agitation process was repeated. The 2 aliquots of water were combined and filtered through a glass wool plug into a separatory funnel, where solvent extraction was performed using 3 X 150 mL aliquots of benzene. This procedure was done in duplicate.

(c) Soxhlet Extraction

Approximately 300 mL benzene were run through the Soxhlet apparatus for 1 hr prior to use, followed by 300 mL water run for several hrs to ensure the removal of contaminants. A 50 g sample of flyash was placed in a coarse porosity

fritted glass extraction thimble and extracted for 48 hr with 500 mL water in a Soxhlet apparatus. After the extraction, the Soxhlet apparatus was dismantled, and the Soxhlet extractor and the outside of the thimble were rinsed with 50 mL water to remove all traces of flyash. This water was added to that already in the round bottom flask. The same glass surfaces were then rinsed with a 50 mL volume of benzene, which was placed in a separatory funnel. The thimble was emptied and all visible traces of flyash were removed by rinsing the thimble under the deionized water tap. The thimble was then used to filter all the water previously collected, which was then transferred to the separatory funnel. Several water rinses of the round bottom flask were also filtered through the thimble into the separatory funnel. The thimble was again rinsed under the tap to remove any particulate matter, then 25 mL benzene were forced through the thimble by applying positive pressure at the top of the thimble with a rubber bulb. The round bottom flask was rinsed several times with a total of 25 mL benzene, which was added to the separatory funnel.

For the extraction at pH 7, deionized water was used and no extra chemical was employed.

For the extraction at pH 4, the water was acidified using formic acid prior to extraction.

For the extraction at pH 10, the water was made basic with 2-methoxyethylamine prior to extraction.

Several refinements to the method described above were made during the course of the experiment.

- i) Boiling beads were placed in the bottom of the round bottom flask before the extraction to prevent bumping. This method change was used only once.

- ii) 400 mL water was used rather than 500 mL in order that there be more room for boiling solvent in the flask.
- iii) A magnetic Teflon stir bar was used in conjunction with a hot plate/stirrer to mix the water constantly. The heating mantle was placed on top of the hot plate/stirrer. The vortex of the water was kept close to the bottom of the flask to ensure good heat transfer.

The extraction was performed in duplicate at each pH condition, and an extraction blank which used the same method but omitted the flyash was also run at each pH condition.

Benzene-Water Partitioning

After the Soxhlet extraction at pH 7, enough benzene was added to the separatory funnel to bring the total volume of benzene to 150 mL, and this volume was used as the first of three 150 mL aliquots of benzene used for solvent extraction. The three aliquots of benzene extract were combined and the volume was reduced to approximately 15 mL by rotary evaporation under aspirator vacuum. The extract was then transferred to a cone bottom flask with a Pasteur pipet, followed by several benzene rinses of the round bottom flask, and the volume was further reduced to approximately 5 mL in the same manner. The top phase in the cone (the benzene phase) along with several benzene rinses were transferred by Pasteur pipet to a small cone bottom flask, taking care not to transfer any of the aqueous phase. The volume in the flask was reduced to approximately 1 mL using rotary evaporation under aspirator vacuum and then transferred with several benzene rinses to a calibrated 1 mL reacti-vial. The volume was reduced to 50 μ L under a gentle stream of high purity nitrogen. The vial was sealed with a screw cap fitted with a Teflon seal, and stored at -15°C .

The pH 4 water extract was neutralized with sodium hydroxide prior to solvent partitioning.

The pH 10 water extract was neutralized with sulfuric acid prior to solvent partitioning.

Several refinements were made to the solvent partitioning step. Instead of 3 X 150 mL aliquots of benzene, the first aliquot was 100 mL and the final two were 50 mL each. Also, during the last step in the concentration, the volume in the reacti-vial was reduced just to the point of dryness and then 20 μ L benzene was added prior to storage at -15°C .

Gas Chromatographic Analysis

GC analyses were carried out on an Hewlett-Packard HP 5880A gas chromatograph equipped with a flame ionization detector (FID) and an electron capture detector (ECD). A cool on-column injector and a 30 m x 0.32 mm I.D. Durabond DB-5 fused silica capillary column (J & W Scientific, Rancho Cardova, CA, U.S.A.) were used for both the FID and ECD analyses. A microcomputer data system and cartridge tape allows storage of chromatographic information for further calculations. The GC conditions for both methods of detection were as follows: injection port temperature at less than 50°C ; column temperature programmed from 80°C to 300°C at $5^{\circ}\text{C}/\text{min}$ with initial 1 min and final 10 min isothermal periods; detector temperature 350°C and helium carrier gas flow rate 3 mL/min at room temperature.

Gas Chromatographic/Mass Spectrometric Analysis

GC/MS analyses were performed using a Hewlett-Packard HP 5987A GC/MS system with an HP 1000 data system and an HP 7914 Winchester disk drive.

For the electron ionization (EI) mode, an ionization voltage of 70 eV and a source temperature of 250°C were used. A direct interface kept at 300°C linked the HP 5880A to the mass spectrometer. Both linear scanning (50-500 amu) and

selected ion monitoring (SIM) were used. Using SIM, it is possible to monitor up to 5 different groups of ions with up to 20 selected ions in each group. The system provided for data acquisition and storage allows the reconstruction of chromatograms at any mass in the scan range. During or after a run, the mass spectrum of any peak on the total ion chromatogram (TIC) trace may be obtained. To help identify compounds by their mass spectra there is a library search system which incorporates a probability based matching system (PBM) based on 70,000 reference spectra as well as a self-training interpretive retrieval system (STIRS).

The column used was a 30 m x 0.25 mm Durabond DB-5 fused silica capillary column (J & W Scientific, Rancho Cordova, CA, U.S.A.). The GC conditions were the same as those used for the GC analysis.

The GC/MS was also operated in the chemical ionization (CI) mode. The reagent gas for CI was methane. The source temperature for positive ion chemical ionization (PICI) was 200°C and it was 100°C for negative ion chemical ionization (NICI).

Dioxin Recovery Study

To determine the extent of the recovery of dioxins in water, the following recovery study was performed.

A benzene solution containing 5.0 ng/ μ L 1234-TCDD and 4.7 ng/ μ L OCDD was diluted to various concentrations. Each solution was used to spike a 250 mL aliquot of water in a round bottom flask. Each aqueous solution was well shaken, and allowed to sit for 30 min. The dioxins were solvent extracted in a separatory funnel with 3 x 100 mL aliquots of benzene. A 25 mL volume of benzene was then used to rinse the round bottom flask and the separatory funnel. All of the benzene was combined and the volume was reduced to approximately 15 mL with rotary evaporation under aspirator vacuum. The extract was transferred to a cone bottom flask with several benzene rinses and the volume was further reduced to

approximately 5 mL by the same method. The organic phase was transferred by Pasteur pipet to a small pear shape flask, along with several benzene rinses, taking care not to transfer any of the aqueous phase. The volume of the benzene extract was reduced to approximately 1 mL by rotary evaporation under aspirator vacuum, and transferred to a 1 mL reacti-vial along with several benzene rinses. The volume of the benzene in the reacti-vial was reduced under a gentle stream of high purity nitrogen just to the point of dryness, and 20 μ L of benzene was added to the vial before sealing it and storing it at -15°C .

Further recovery studies were performed on a PCDD standard mixture containing 1234-TCDD; 12347-P₅CDD; 123478-H₆CDD, and 1234678-H₇CDD, all at concentrations of approximately 50 ppb in benzene. A 10 μ L volume of this solution was used to spike a 250 mL volume of water to give a final concentration for each dioxin component of approximately 2 ppt. The flask was shaken and allowed to sit for 30 min, then solvent extracted in a separatory funnel with 2 x 50 mL aliquots of benzene. A 25 mL volume of benzene was used to finally rinse the separatory funnel, then the total volume of benzene was reduced to dryness in the manner described above and diluted to 20 μ L with benzene.

To determine the recovery of dioxins in water, each sample and respective standard was injected on the HP 5880 GC using ECD detection. The only difference in chromatographic conditions from those previously described was the temperature program which was as follows: 80°C to 200°C at $20^{\circ}\text{C}/\text{min}$ then programmed from 200°C to 300°C at $6^{\circ}\text{C}/\text{min}$. There were 1 min initial and 5 min final isothermal periods.

The corresponding peak areas of the various dioxin standards were used to determine the percentage of dioxin recovered by the solvent extraction. The following equation was used.

Once the detection limit of GC/ECD was reached, the recovery study was performed in duplicate.

$$\% \text{ dioxin recovery} = \frac{\text{area of extract peak}}{\text{area of standard peak}} \times \frac{a}{b} \times \frac{c}{d} \times 100$$

a = volume injected of standard

b = volume injected of extract

c = dioxin concentration in standard solution

d = dioxin concentration in extract (assuming 100% recovery).

RESULTS AND DISCUSSION

Soxhlet Extraction and Benzene-Water Partitioning

Three methods were used for the leaching study of flyash with water. These included a manual and ultrasonic agitation of flyash-water mixture, and Soxhlet extraction of flyash with water. The details of methods have been described in the experimental section. Most organic compounds which have been found in flyash exhibit very low solubilities in water. To remove a sufficient amount of organic compounds from flyash for the following analysis, a large amount of water is needed and highly efficient contact between water and flyash must be achieved. In practice, those requirements are difficult to fulfill using the manual and ultrasonic agitation methods. Few organic compounds were found in the water samples treated by these two methods. PCDD and PCDF were not detected in these samples. In addition, the analytical results obtained from these two methods were irreproducible due to the manual operation. To provide a more exhaustive and reproducible extraction a Soxhlet extraction was finally used for the leaching study. Figure 1 is a schematic diagram showing the sample preparation procedure and the subsequent analysis of PCDD, PCDF, and other organic compounds in water.

In nature, there is a constant circulation of water - vapourization, condensation and precipitation. This circulation is similar to the basic process of a Soxhlet extractor. Therefore, the Soxhlet extraction of flyash with water is a good simulation of leaching flyash with water in nature. In a thimble, flyash always contacts fresh water which is condensed. By recycling, a significant amount of organic compounds can be gradually removed from the flyash, even those with low solubilities in water. A relatively small amount of water provides a highly efficient extraction of organic compounds in a Soxhlet extraction procedure. Eventually, organic compounds removed from flyash can be accumulated in

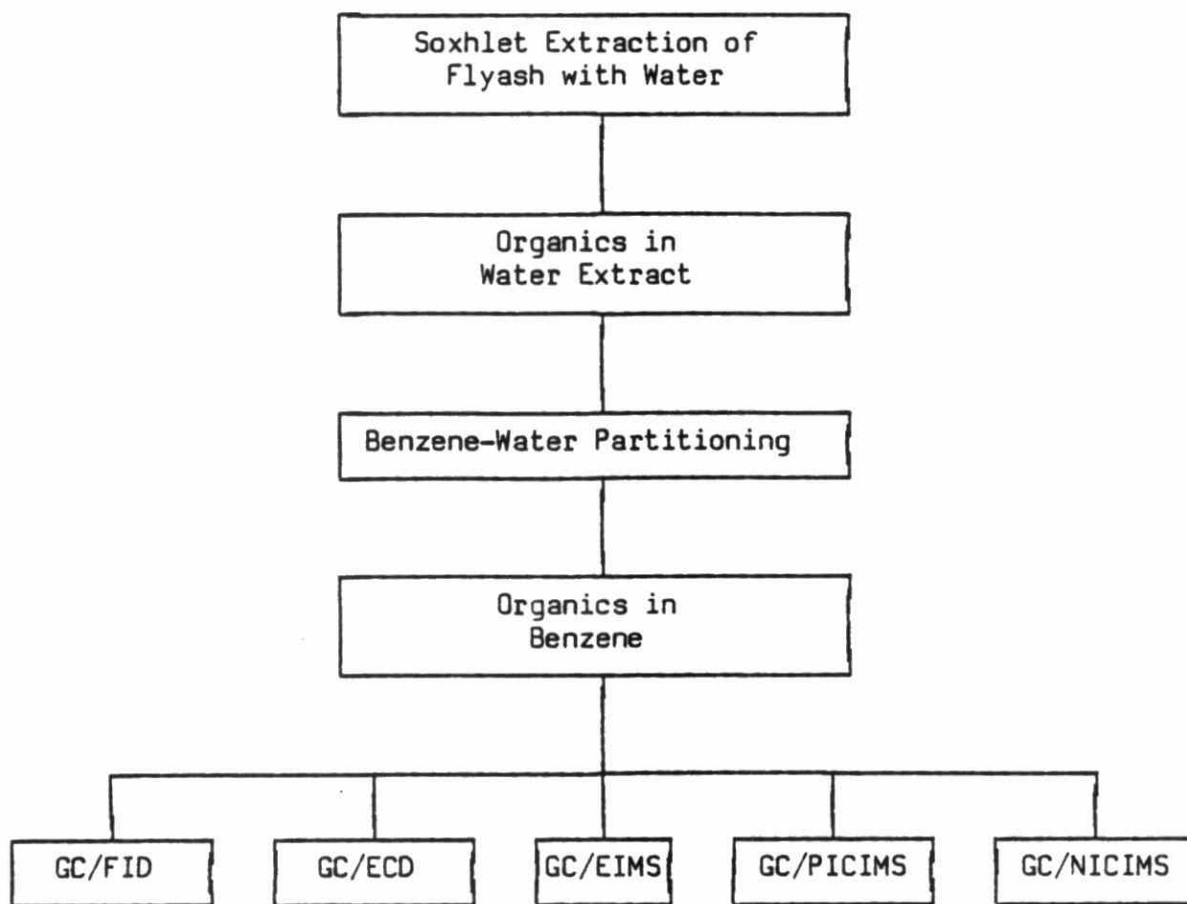


Figure 1: Scheme diagram showing sample preparation procedure and subsequent analysis

the water extract to a detectable quantity. This also reflects the phenomenon of nature, in which the organic compounds are gradually leached away by water from the flyash.

In contrast to the low solubility of organic compounds in water, many trace organic compounds have a strong tendency to adsorb on a glass surface. When large glass surface areas are involved in a water sample preparation, the loss of organic compounds due to such adsorption could be significant. This loss usually leads to low recovery and poor reproducibility. Furthermore, some trace organic compounds may be below the limit of detection owing to the adsorption. It has been found in this study that trace PCDD and PCDF adsorb strongly on glass surfaces. This adsorption problem has been effectively minimized using a Soxhlet extractor rather than the large volume glassware apparatus required when a large amount of water is involved. In addition, all glassware surfaces which made contact with the water extract were carefully rinsed with benzene, and then these benzene aliquots were collected for organic compound analysis. However, during the entire sample preparation, direct contact of flyash with benzene was prevented to ensure that the organic compounds found were removed from the flyash solely by water.

A simple benzene-water partitioning procedure was used to transfer the organic compounds from the water extracts into benzene for the subsequent analysis. This method minimizes the loss of trace organic compounds that usually occurs during a complicated procedure, and also provides a high transfer efficiency due to the greater solubility of most organic compounds in benzene compared to water.

Dioxins Found in Water Extracts

A total of 14 Soxhlet extractions of flyash were carried out at pH 4, 7,

and 10. Those 14 extracts were analyzed for PCDD and PCDF after benzene-water partitioning. The analytical techniques used included GC/ECD, GC/EIMS, GC/NICIMS, and GC/PICIMS. The results of PCDD detection are summarized in Table I. In these 14 water extracts, PCDD were detected in 8 samples by GC/ECD, and were more positively identified in 3 samples by GC/EIMS and GC/NICIMS.

GC/ECD analysis provided high sensitivity, in the pg range for PCDD and PCDF. However, because of the presence of interfering compounds in the water extract, tetrachlorodioxins (TCDD) and pentachlorodioxins (P_5 CDD) could not be positively identified on the GC/ECD chromatograms for some samples. There were less interfering peaks in the elution region of hexachlorodioxins (H_6 CDD), heptachlorodioxins (H_7 CDD), and octachlorodioxin (OCDD) on the GC/ECD chromatograms. Therefore, a typical pattern of H_6 CDD, H_7 CDD and OCDD, which was usually observed in a benzene-extract of flyash, could be easily recognized on a GC/ECD chromatogram of the extract sample containing PCDD. Figure 2 shows a typical GC/ECD chromatogram of the water extraction sample containing PCDD. A corresponding GC/ECD chromatogram of an extraction blank is shown in Figure 3. No PCDD impurities were found in this blank. Finding dioxins by GC/ECD in Table 1 refers to detection of at least one of H_6 CDD, H_7 CDD and OCDD. For most samples more than one of the PCDD were identified by GC/ECD.

The GC/MS system used in this study had a lower sensitivity for PCDD determination than GC/ECD. GC/MS with selected ion monitoring (GC/MS/SIM) was used with electron impact ionization (GC/EIMS/SIM) and with negative ion chemical ionization (GC/NICIMS/SIM). PCDD and PCDF were identified in three water extraction samples by GC/EIMS/SIM and/or GC/NICIMS/SIM. Since two characteristic ions, [M] and [M+2], were monitored for each PCDD and PCDF congener the presence of PCDD and PCDF, indicated by GC/MS analysis, is reasonably positive. Figures 4 and 5 illustrate the GC/MS/SIM data of a water extract of flyash, showing

TABLE I Number of Water Extraction Samples in Which PCDD
Were Found at Concentrations Less Than 10 ppt

pH	number of extracts	number of samples in which PCDD were detected		
		GC/ECD	GC/EIMS	GC/NICIMS
4	5	2	1	1
7	7	5	2	2
10	2	1	-	-

note: ND - non-detectable at the instrument detection limit

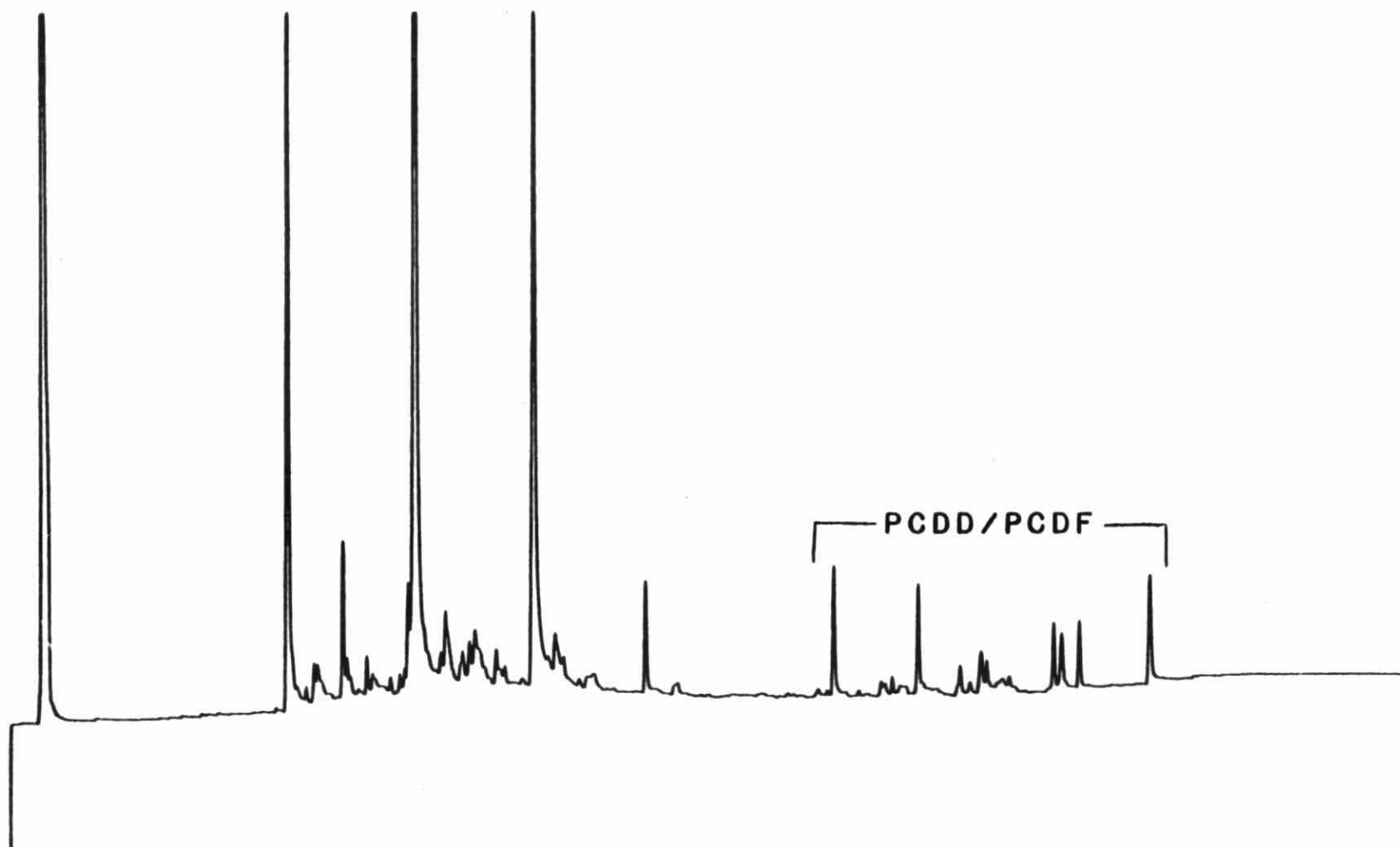
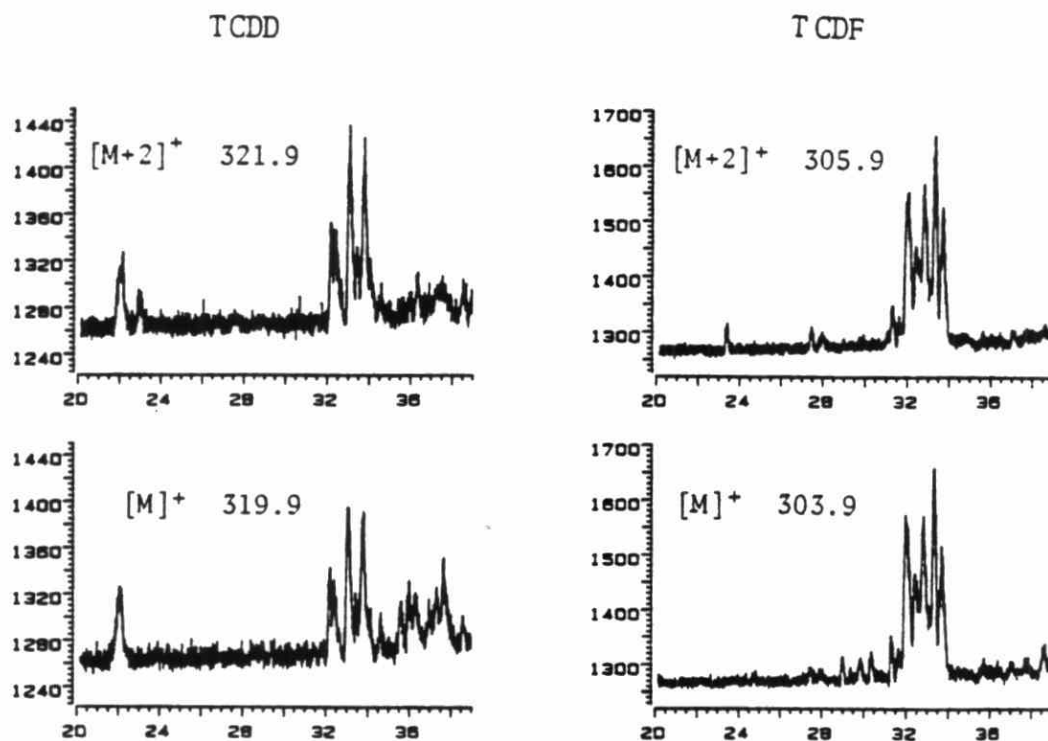


Figure 2: GC/ECD chromatogram of a water extraction
sample containing PCDD/PCDF



Figure 3: GC/ECD chromatogram of an extraction blank.

LF-7-5



LF-7-5

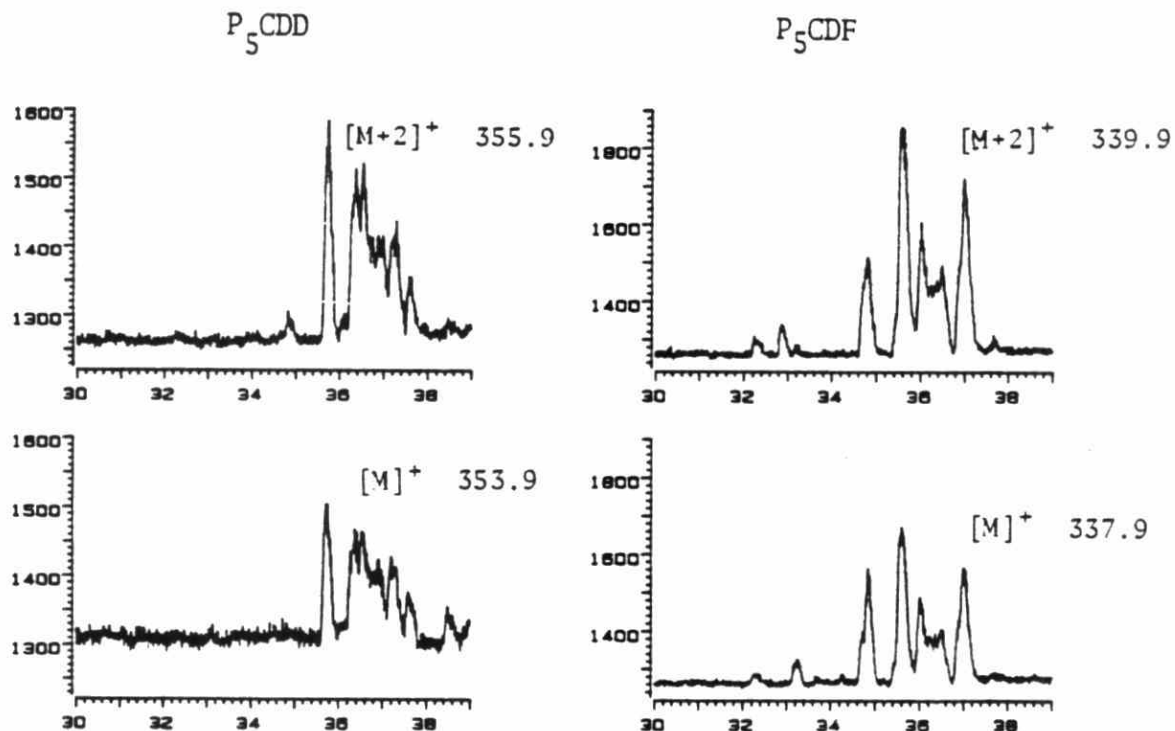
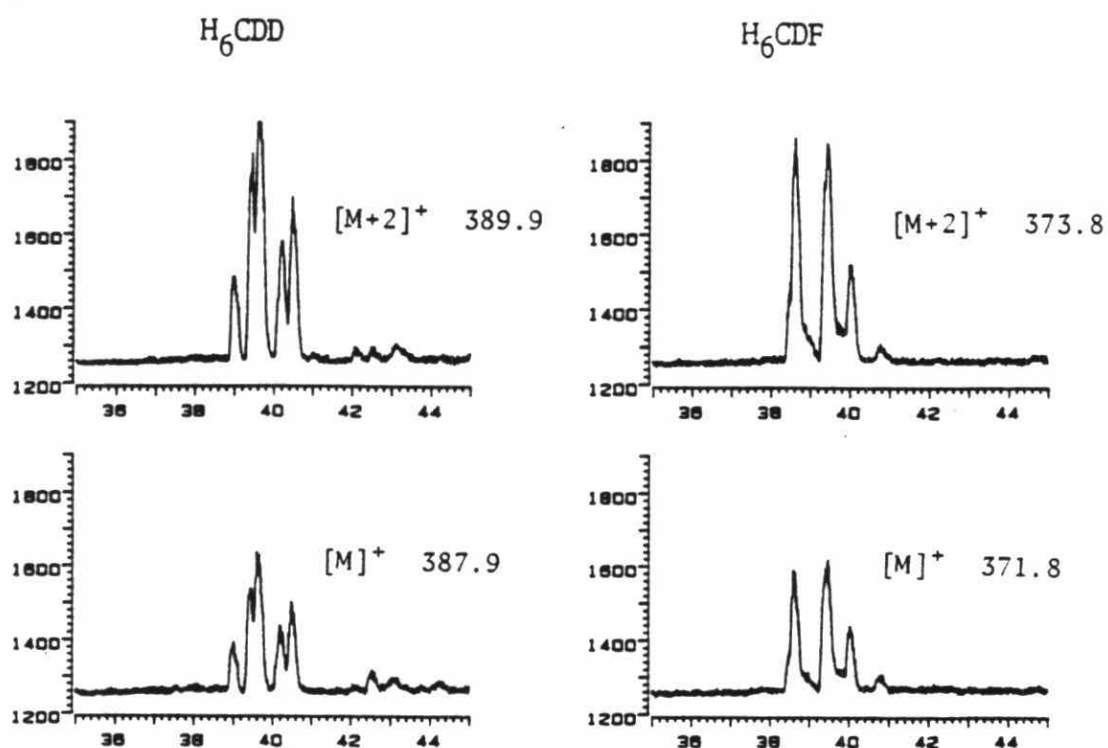


Figure 4: GC/EIMS/SIM data showing evidence of PCDD and PCDF in water extracts

LF-7-5



LF-7-6

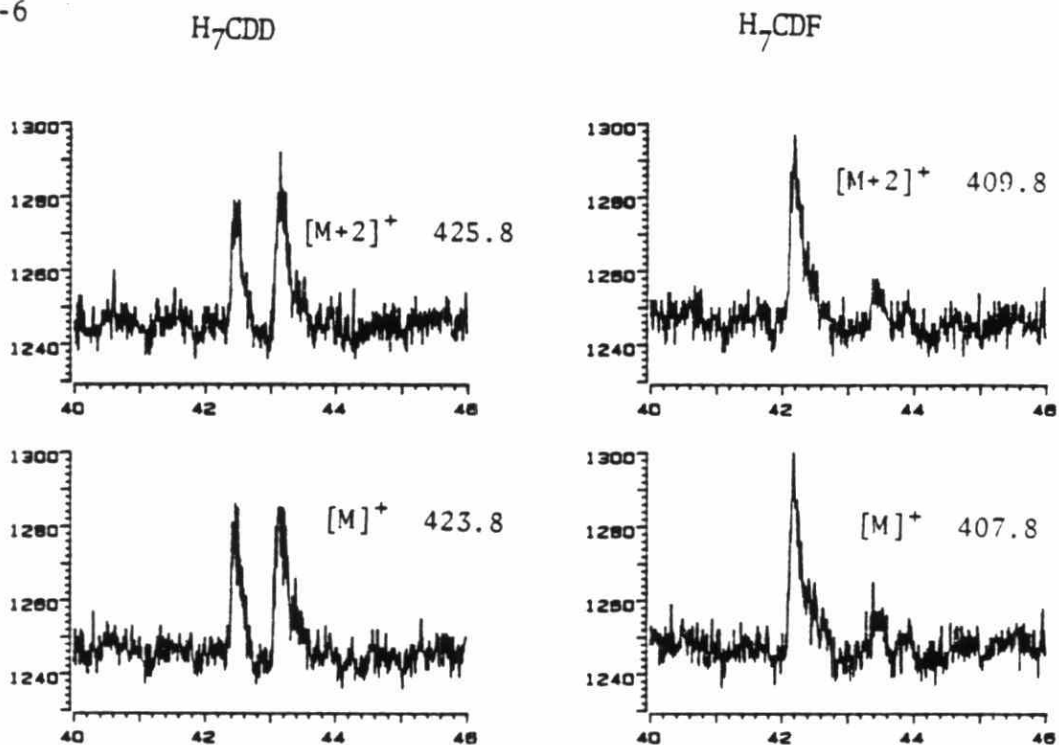


Figure 4 (continued)

LF-4-2

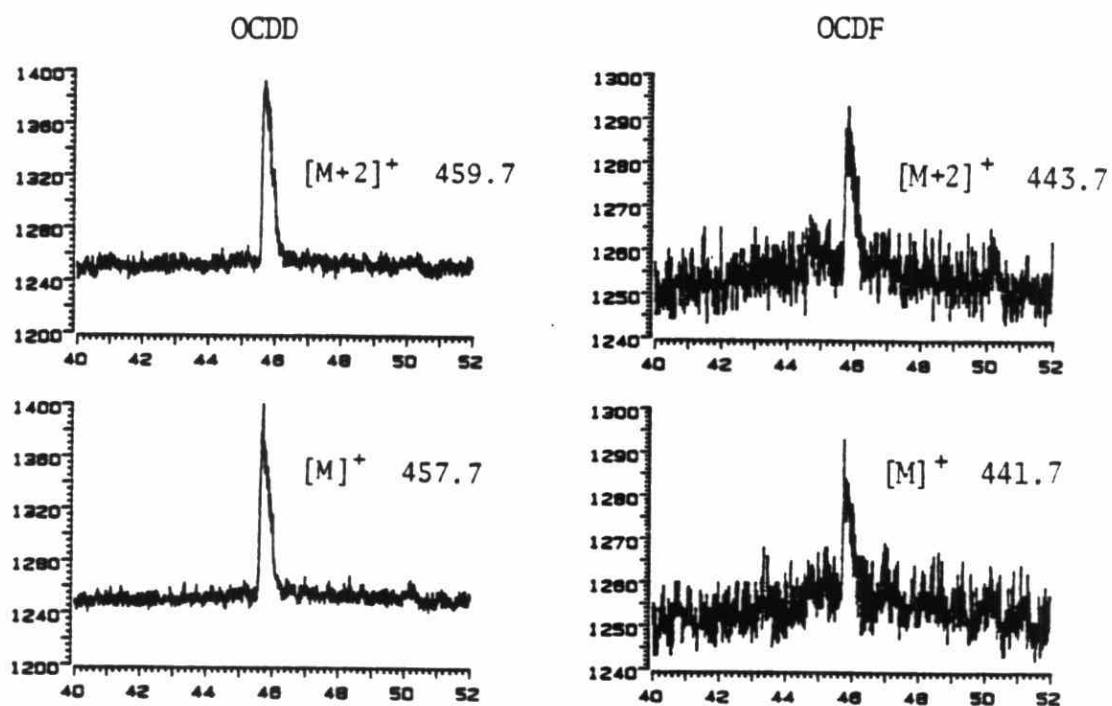
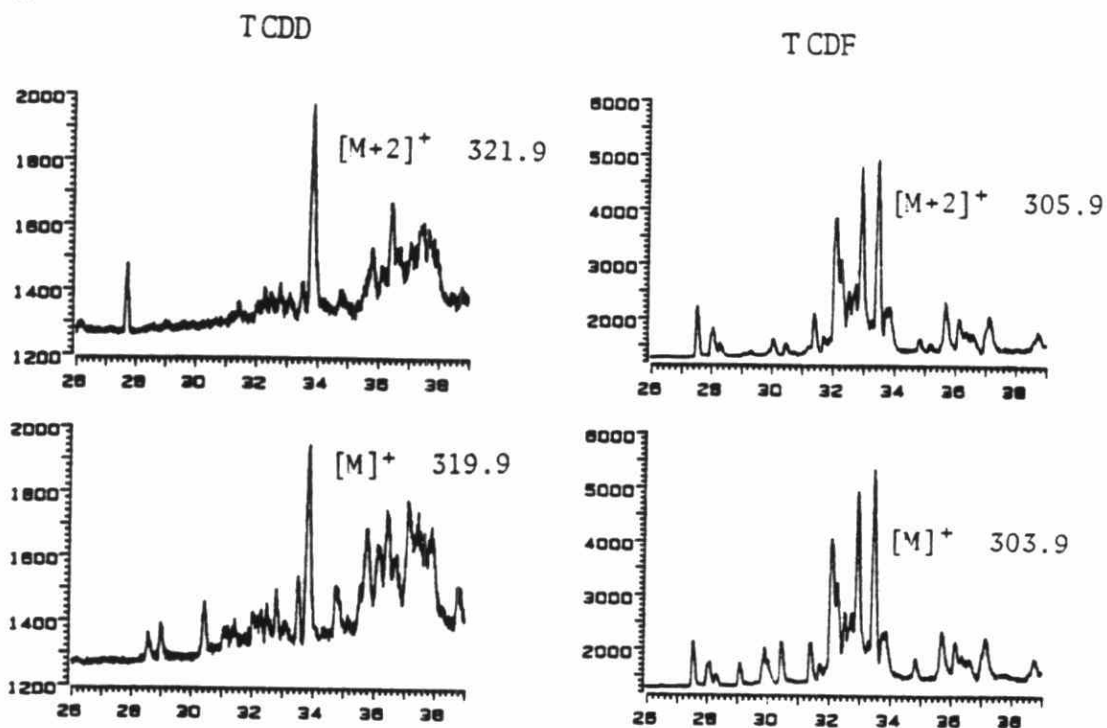


Figure 4 (continued)

LF-7-5



LF-7-6

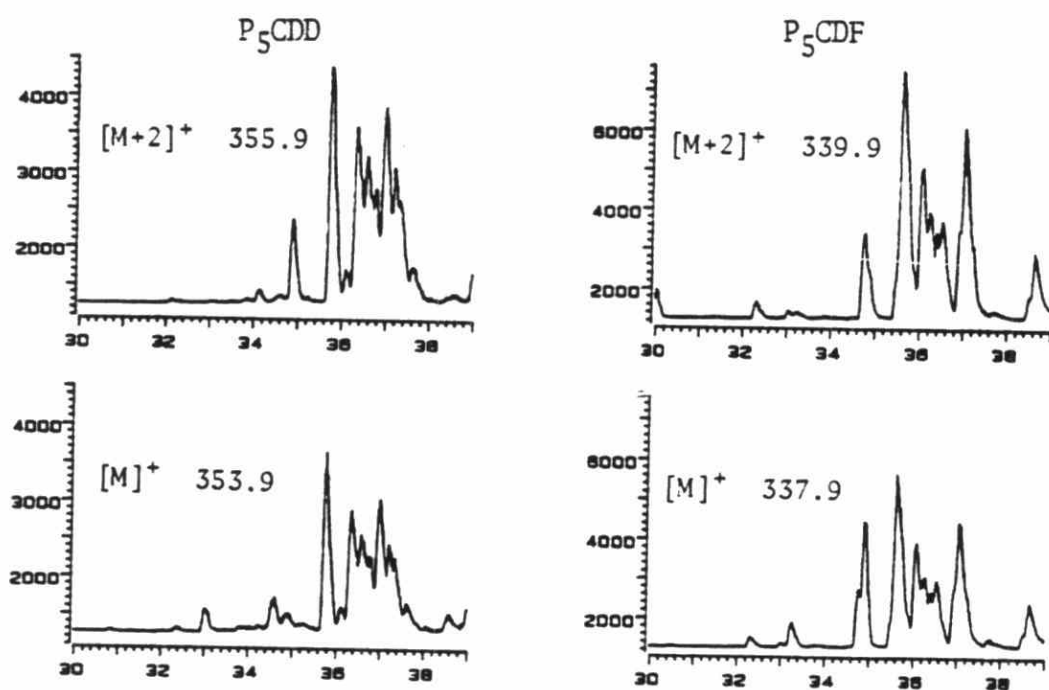
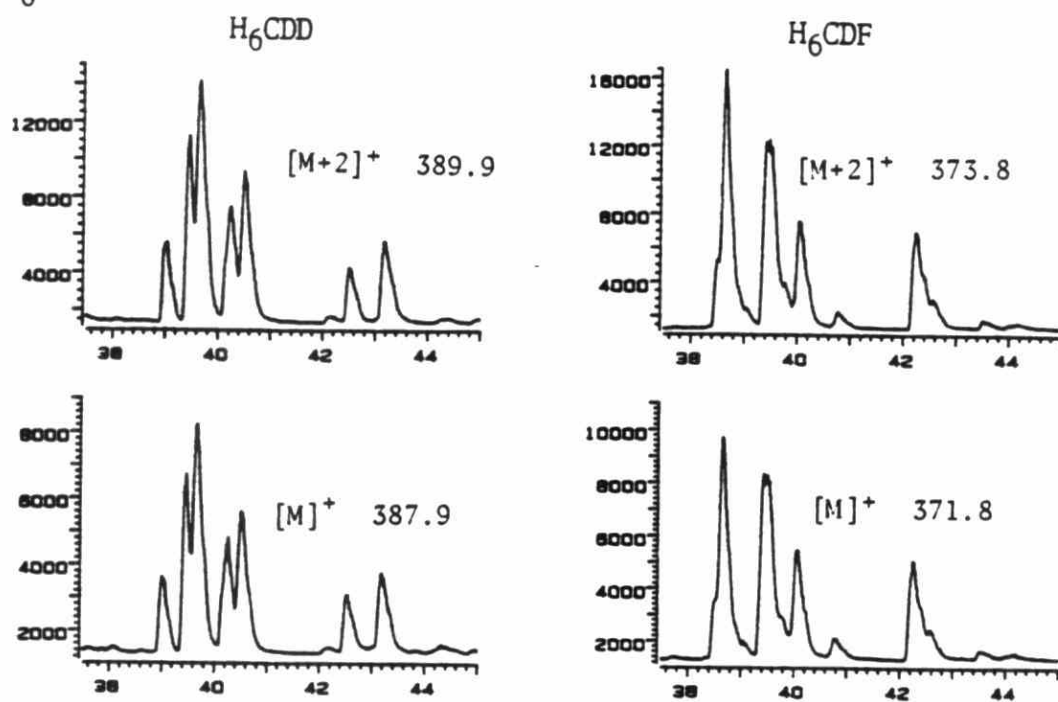


Figure 5: GC/NICIMS/SIM data showing evidence of
PCDD and PCDF in water extracts

LF-7-6



LF-4-2

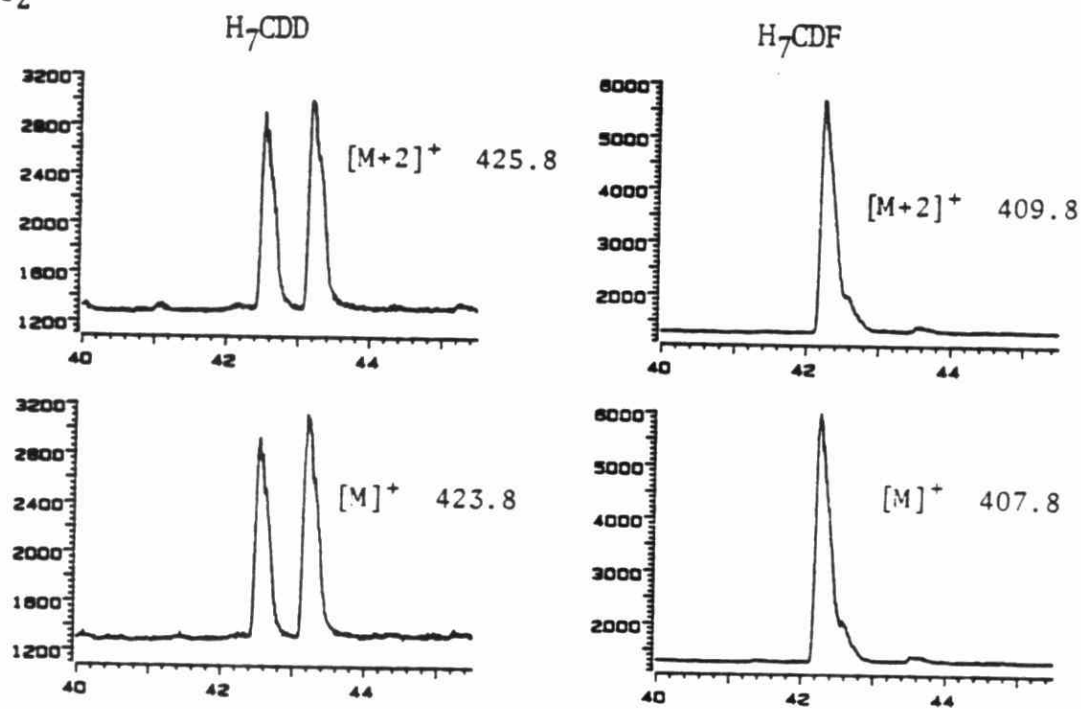


Figure 5 (continued)

LF-4-2

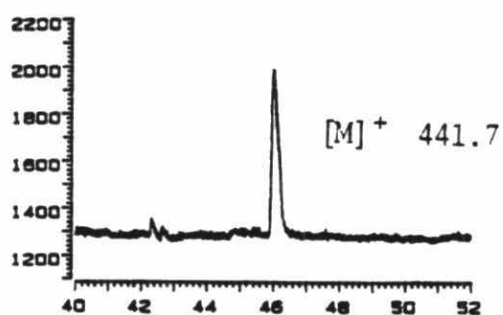
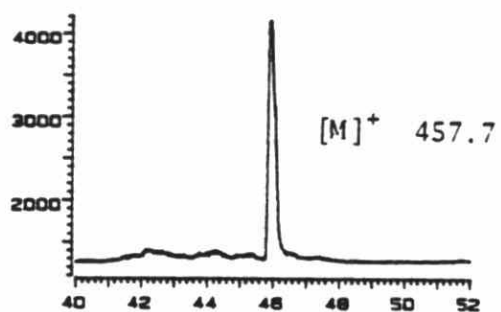
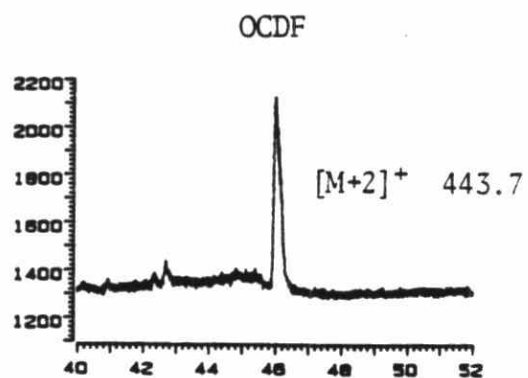
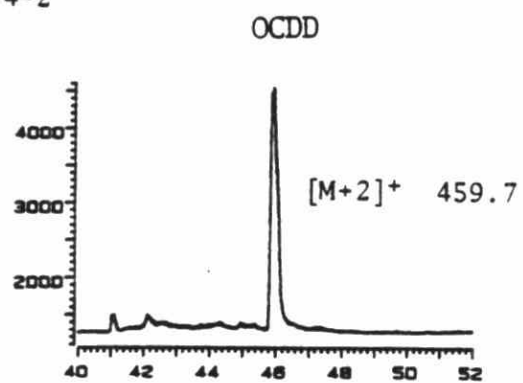


Figure 5 (continued)

evidence that PCDD and PCDF are present in water extraction samples. Figure 6 shows the GC/MS/SIM data of a water blank obtained from the same preparation procedure. No PCDD or PCDF were found in the water blank.

A large variation exists in the concentrations of PCDD and PCDF found among these 14 extraction samples. This is most likely caused by the instability of trace amounts of PCDD and PCDF in water, and also by the problems encountered in an analysis at the ppt level. The differences among flyash samples from batch to batch could be another reason for the deviation. Therefore, quantification of PCDD and PCDF in all the water extracts was not attempted in this study. Based on the results obtained from some samples, the concentration of PCDD leached into water is estimated to be in the 1 to 400 ppt range as shown in Table II.

The recovery of PCDD using reference standards in the benzene-water partitioning procedure was investigated. The concentration level of PCDD standards in water was progressively lowered to the detection limit of GC/ECD. Due to interferences, this recovery study was limited to H_6CDD , H_7CDD , and $OCDD$ standards. GC/MS was not used because of the greater sensitivity provided by the electron capture detector. The recovery data given in Table II show a good recovery of PCDD at the 2 ppt level.

Based on the results obtained both from the analysis of PCDD in water extracts and study of PCDD recovery, two conclusions can be reached. First, PCDD and PCDF can be leached from flyash by water at pH 4, 7, and 10. It is slightly easier to extract PCDD and PCDF into water at pH 7. Second, the precise quantity of PCDD and PCDF leached by water from flyash is difficult to determine because the levels of PCDD and PCDF are very low, and at such low levels, their tendency to adsorb onto glassware can present a significant loss.

SOX-7-BLANK EI SIM
TIC

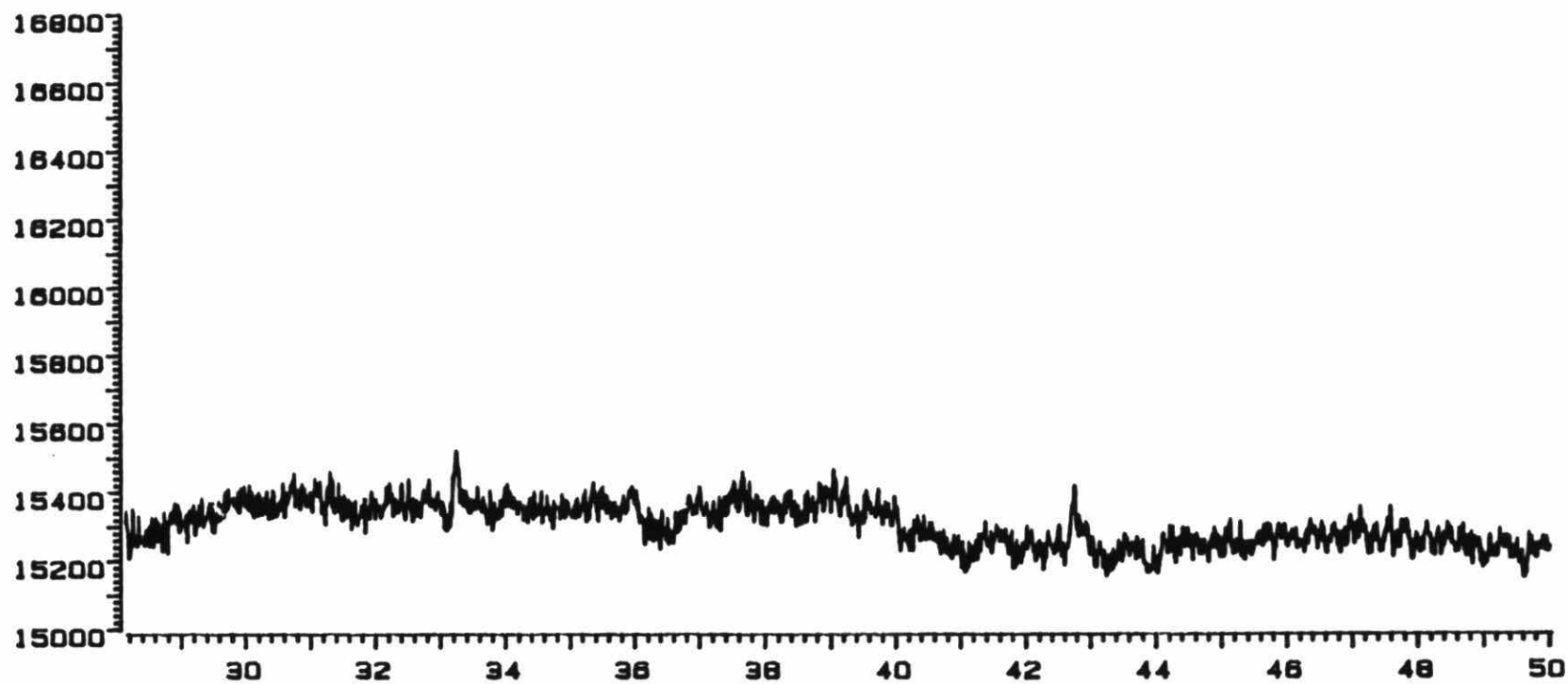


Figure 6: GC/EIMS/SIM data of water extraction blank,
monitoring at $[M]^+$ and $[M+2]^+$ for PCDD and PCDF

Table II Concentration of PCDD Extracted in Water
from Flyash (parts-per-trillion)

sample	method of determination	TCDD	P ₅ CDD	H ₆ CDD	H ₇ CDD	OCDD
LF-7-5 ¹	GC/NICIMS/SIM	5.45	106.3	301.3	360.5	212.8
	GC/EIMS/SIM	53.6	136.8	219.1	265.6	132.3
	GC/ECD	IN	IN	125.7	153.8	335.6
LF-7-6	GC/EIMS/SIM	ND	ND	ND	69.0	50.7
	GC/ECD	IN	IN	40.8	43.1	251.7
LF-4-2	GC/NICIMS/SIM	2.0	6.0	13.2	19.5	19.7
	GC/EIMS/SIM	ND	13.3	12.8	42.9	15.6
	GC/ECD	IN	IN	69.6	62.3	107.9
LF-7-7	GC/ECD	IN	IN	17.2	8.3	5.7
LF-4-1	GC/ECD	IN	IN	4.7	7.6	10.3
LF-10-1	GC/ECD	IN	IN	54.5	ND	22.2

Note: IN - unable to quantify due to interferences
 ND - non-detectable at the instrument detection limit
¹ - LF refers to the study "Leaching of Flyash". The first number refers to the pH of the leachate and the second number refers to the experimental trial number.

TABLE III Recovery of PCDD Standards in
Benzene-Water Partitioning

concentration level	compound	recovery (%)
2 ppt	OCDD	80
2 ppt	H ₇ CDD	61
2 ppt	H ₆ CDD	98

Identification of Organic Compounds in Water Extracts

In this study many organic compounds have been found in the water extracts. Five analytical techniques were used for such analysis. They included GC/FID, GC/ECD, GC/EIMS, GC/PICIMS and GC/NICIMS. The identification of most compounds was based on the data obtained from the three GC/MS analyses. The data of GC/FID and GC/ECD were used to facilitate the identification for some compounds.

A combination of GC/EIMS, GC/PICIMS, and GC/NICIMS analyses provided a wealth of information for compound identification. Three total ion chromatograms (TIC) obtained from these three GC/MS methods of analyses for one water extract of flyash are illustrated in Figure 7. Although the same chromatographic conditions were used, these three total ion chromatogram (TIC) traces have different appearances. Some components that show no peaks on the GC/EIMS traces have good mass spectra using GC/NICIMS. The mass spectra obtained from the three GC/MS methods of analysis for a compound are complementary, facilitating compound identification. Such an example is given in Figure 8. Based on the EI mass spectrum (a), the most probable molecular weight of the unknown compound could be 254 or 177. However, a MW of 254 can be positively confirmed using the PICI mass spectrum (b) and NICI mass spectrum (c). The retention index obtained from GC/FID and GC/EIMS analyses indicates the unknown could be phenylphenanthrene or phenylanthracene. The spectra of NICIMS most likely rejects the possibility of the unknown compound being phenylanthracene because anthracene exhibits no response to NICIMS (5). Therefore, this unknown compound is tentatively identified as phenylphenanthrene. Utilizing the information of five analytical techniques, many compounds have been identified in the water extracts obtained at the different pH ranges studied.

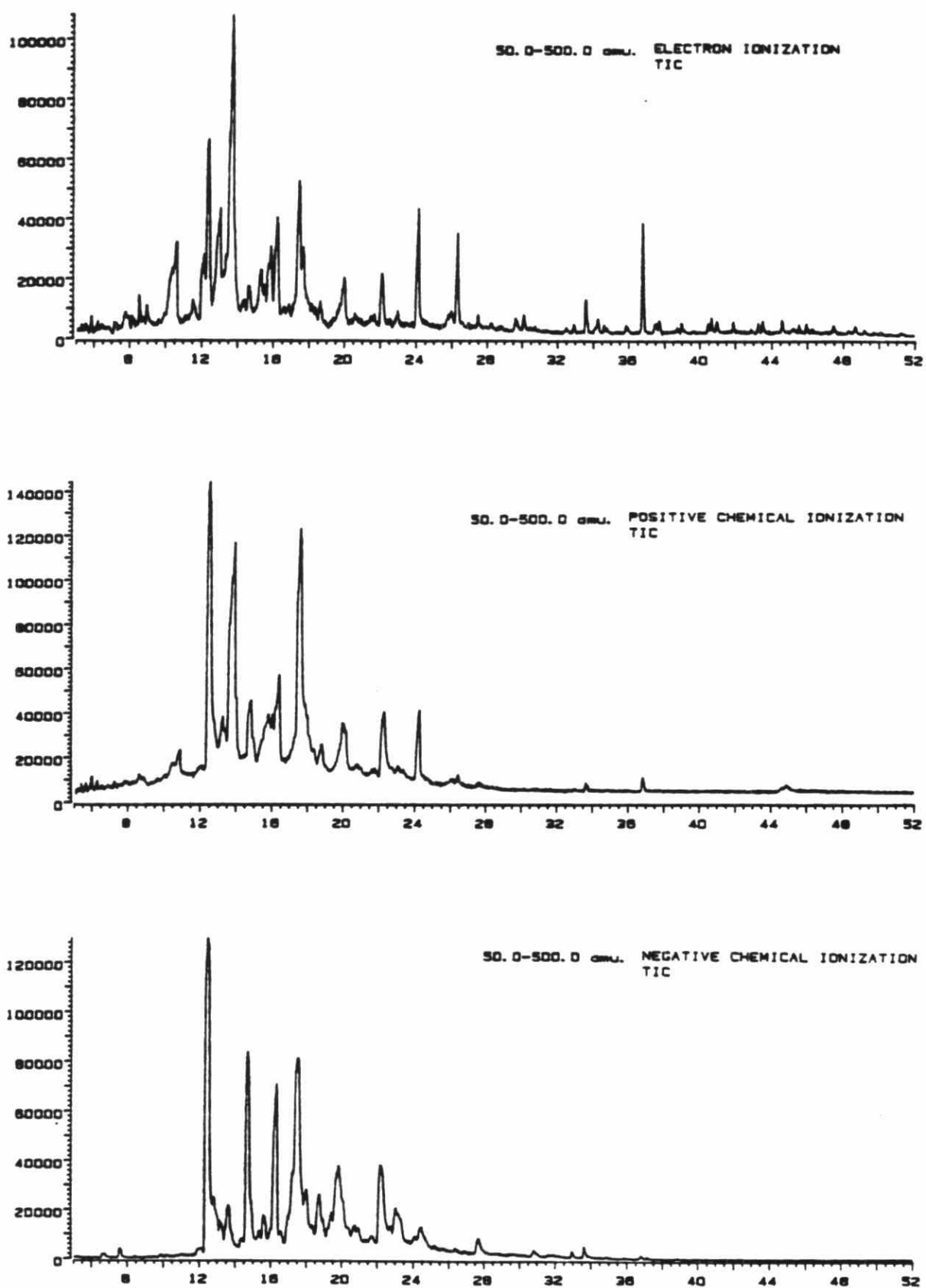


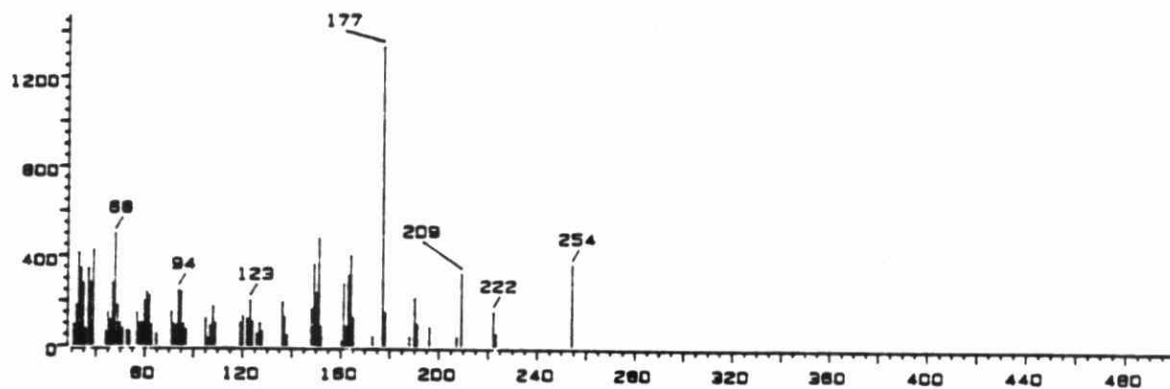
Figure 7: Total ion chromatogram traces of one water extract (pH 10) analyzed by GC/MS with three ionization methods.

File >Y1464
8pk Ab 1336

LF-10-2-4

LF-10-2-4 (20uL) EILIN

Scan 1875
34.88 min.

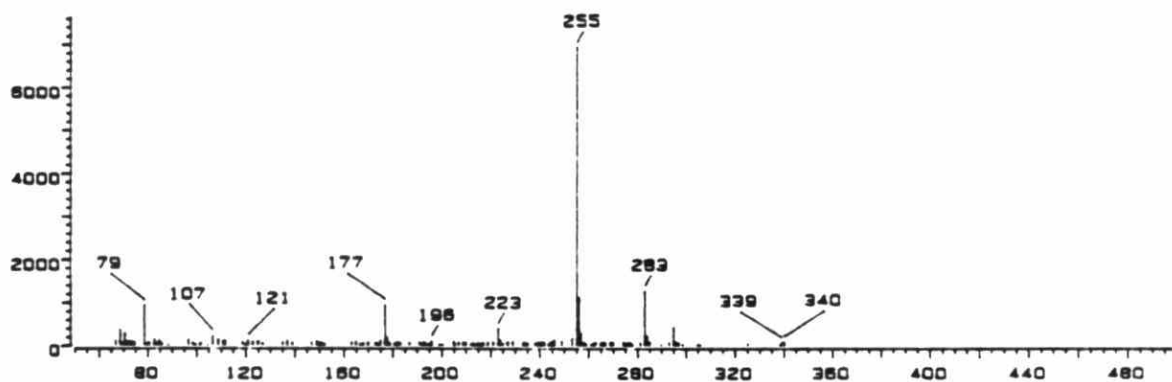


File >Y1745
8pk Ab 5941

LF-10-2

PCI

Scan 1842
33.91 min.



File >Y1500
8pk Ab 1149

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 1875
34.90 min.

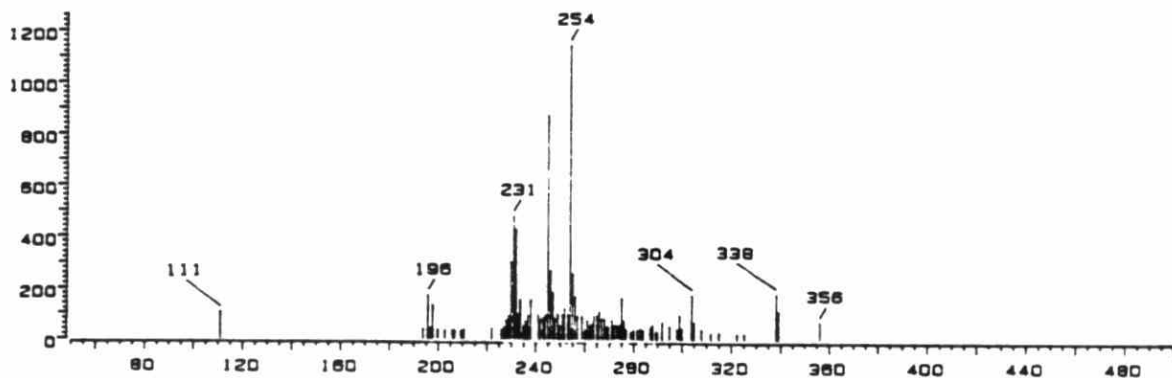


Figure 8: Mass spectra of an unknown compound in water extract sample
(a) obtained from GC/EIMS; (b) obtained from GC/PICIMS; and
(c) obtained from GC/NICIMS

Organic Compounds Found in Water Extracts of Different pH

Leaching flyash with water was studied at acidic (pH 4), neutral (pH 7) and basic (pH 10) conditions. Those three conditions chosen cover a normal pH range water including natural and discharged water from different waste sources. The number of suitable acids and bases that could be used in a Soxhlet extraction is limited. Not only does the acid or base have to be water soluble, but it also has to have a boiling point close to that of water so it will evaporate and carry up the condensor of Soxhlet extractor in the same manner as water. In such a way, the water in the extraction thimble remains at the proper pH condition. To keep the pH values of water in the thimble at pH 4 and 10, formic acid and 2-methoxyethylamine were used in the Soxhlet extractions, respectively. These two chemicals have boiling points similar to that of water. After the Soxhlet extraction, water extracts were neutralized before the benzene-water partitioning procedure.

Figure 9 shows the GC/FID traces of organic compounds in the water extracts obtained at pH 4, 7, and 10. The organic compounds present in water are different depending on the pH of water. Tables IV, V and VI list the organic compounds found in water extracts obtained at pH 4, 7, and 10, respectively. Many organic compounds have been identified using the methods mentioned above. However, some cannot be identified based on the available information. For those unidentified compounds, molecular weight values and some information regarding their constituents are listed in these tables based on the GC/MS data. The PICI and NICI mass spectra of some unidentified compounds are given in the Appendix.

Many nitrogen-containing compounds and hydroxy-containing compounds were found in the water extracts. Some of them have not been found in the benzene extract of flyash. Comparing the GC/FID traces in Figure 9, more component peaks have been seen in the water extracts of pH 10, and less in those of pH 4. Nitro-

TABLE IV Compounds Found in Water Extract of pH 4

no.	compound	scan number	MW	MS method ^a
1	ui ^b	21	126	P
2	ui	34	106	P
3	ui	56	108	P
4	ui	75	126	P
5	dimethyl phenol	92	122	
6	dichloropropenamide	99	139	
7	ui	111	115	P
8	ui	133	127	N
9	3,4-dimethyl-3-hexen-2-one	136	126	
10	octene alcohol	151	128	
11	ethyl benzene	158	106	
12	ui	172	142	P
13	dichloro butadiene	198	132	
14	ui	206	108	P
15	octene ketone	238	126	
16	ui	258	140	N
17	ui	284	138	N
18	tetrachloro pentene	301	206	
19	ui	311	127	P
20	ui	421	128	N
21	ui	433	168	N
22	bromobutanol	446	152	
23	ui	459	134	P
24	trichlorophenol	465	196	
25	ui	483	148	P
26	trichlorophenol	496	196	
27	ui	508	166	P
28	phthalate	535	bp 149 ^c	N
29	C ₅ -phenol	554	164	
30	2-ethyl biphenyl	644	182	

Table IV (continued)

no.	compound	scan number	MW	MS method
31	ethenyl tetrochloro benzene	668	240	
32	ui	649	218	N
33	ui phthalate	651	bp 149	P
34	trichlorocresol	662	210	
35	acenaphthene	680	154	
36	dimethoxy benzaldehyde	705	166	
37	pentachloro benzene	725	248	
38	ui	767	164	N
39	tetrachlorophenol	787	230	
40	amino-dimethylindan	798	161	
41	diethyl phthalate	840	222	
42	dichlorobenzamide	867	189	
43	ui	867	176	N
44	methyl benzenedicarboxylic acid	927	180	
45	ui	959	174	P
46	dimethyl trichloro biphenyl	1076	284	
47	ui	1038	198	P
48	ui trichloro N-compound ^d	1134	223	N
49	ui trichloro N-compound	1184	223	N
50	caffeine	1202	194	
51	ui trichloro N-compound	1215	223	N
52	ui	1375	294	N
53	ui tetrachloro N-compound	1422	257	N
54	dimethoxy phenanthrene	1621	238	
55	ui pentachloro N-compound	1677	291	N
56	ui pentachloro N-compound	1675	291	N
57	ui	1799	312	N
58	dioctyl phthalate	2000	310	

Table IV (continued)

no.	compound	scan number	MW	MS method
aliphatic hydrocarbons				
59	$C_{14}H_{30}$		198	FID
60	$C_{15}H_{32}$		212	FID
61	$C_{16}H_{34}$		226	FID
62	$C_{17}H_{36}$		240	FID
63	$C_{18}H_{38}$		254	FID
64	$C_{29}H_{60}$		408	FID
65	$C_{30}H_{62}$		422	FID
66	$C_{31}H_{64}$		436	FID
67	$C_{32}H_{66}$		450	FID
68	$C_{33}H_{68}$		464	FID
69	$C_{34}H_{70}$		478	FID
70	$C_{35}H_{70}$		492	FID
71	$C_{36}H_{74}$		506	FID

Note:

a - mass spectra used to obtain MW, P-PICIMS, N-NICIMS

b - ui - unidentified compound

c - bp. base peak in mass spectrum

d - nitrogen containing compound

FID - identification based on GC/FID data

Table V: Compounds Found in Water Extract of pH 7

no.	compound	scan number	MW	MS method ^a
1	uib	21	126	P
2	ui	37	128	P
3	ui	57	108	P
4	ui	77	126	P
5	ui	93	122	P
6	dichloropropenamide	102	139	
7	octene ketone	136	126	
8	ethyl benzene	159	106	
9	ui	224	156	P
10	tetrachloropentene	302	206	
11	ui	321	128	N
12	ui	341	158	P
13	ui	366	158	P
14	trichlorophenol	438	196	
15	trichlorophenol	465	196	
16	ui	516	172	P
17	ui	539	170	N
18	hydroxy methoxy benzaldehyde	551	152	
19	ethenyl tetrachlorobenzene	606	240	
20	trichlorocresol	664	240	
21	ui	677	168	P
22	dimethoxy benzaldehyde	689	166	
23	dimethyl phthalate	714	194	
24	tetrachlorophenol	784	230	
25	ui	815	240	N
26	dichloroethenyl methyl benzene or its isomer	860	186	
27	dichlorobenzamide	903	189	
28	methyl benzene dicarboxylic acid	929	180	
29	dimethyl biphenyl	941	182	
30	dichlorobenzamide	945	189	
31	ui	986	200	N

Table V (continued)

no.	compound	scan number	MW	MS method
32	ui	986	200	N, P
33	pentachlorophenol	1078	264	
34	ui	1131	199	N
35	caffeine	1205	194	
36	ui trichloro N-compound ^d	1219	223	N
37	ui tetrachloro N-compound	1423	257	N
38	dimethoxy phenanthrene	1620	238	
39	ui	1756	336	N
40	ui	1798	312	N
41	dioctyl phthalate	1995	390	
42	pentachlorochrysene	2022	404	
aliphatic hydrocarbons				
43	C ₁₄ H ₃₀		198	FID
44	C ₁₅ H ₃₂		212	FID
45	C ₁₆ H ₃₄		226	FID
46	C ₁₇ H ₃₆		240	FID
47	C ₁₈ H ₃₈		254	FID
48	C ₁₉ H ₄₀		268	FID
49	C ₂₀ H ₄₂		282	FID
50	C ₂₁ H ₄₄		296	FID
51	C ₂₂ H ₄₆		310	FID
52	C ₂₅ H ₅₂		352	FID
53	C ₂₆ H ₅₄		366	FID
54	C ₂₇ H ₅₆		380	FID
55	C ₂₈ H ₅₈		394	FID
56	C ₂₉ H ₆₀		408	FID
57	C ₃₀ H ₆₂		422	FID
58	C ₃₁ H ₆₄		436	FID
59	C ₃₂ H ₆₆		450	FID
60	C ₃₃ H ₆₈		464	FID

Table V (continued)

no.	compound	scan number	MW	MS method
61	$C_{34}H_{70}$		478	FID
62	$C_{35}H_{72}$		492	FID
63	$C_{36}H_{74}$		506	FID
64	$C_{37}H_{76}$		520	FID

Note: see Table IV

TABLE VI Compounds Found in Water Extract of pH 10

no.	compound	scan number	MW	MS method ^a
1	ui ^b	22	145	P
2	methoxy methyl benzonitrile	172	147	
3	ui	267	126	P
4	ui	354	159	P
5	trichlorophenol	468	196	
6	hydroxybiphenyl or its isomer	453	170	
7	methyl biphenylamine	516	183	
8	hydroxy methoxy benzaldehyde	504	152	
9	ethenyl tetrachlorobenzene	613	240	
10	ui	572	153	P
11	diphenylmethane/methyl biphenyl	626	168	
12	trichlorocresol	665	210	
13	dimethoxy benzaldehyde	700	166	
14	N-ethyl naphthaleneamine	704	171	
15	tetrachlorophenol	808	230	
16	tetrachlorophenol	754	230	
17	dichloro ethenyl methyl benzene	873	186	
18	ui	819	204	P
19	dichlorobenzamide	915	189	
20	ui N-compound ^c	987	205	N
21	dichlorobenzamide	1029	189	
22	pentachlorophenol	1086	264	
23	ui trichloro N-compound	1147	223	N
24	methyl phenyl indole	1208	207	
25	caffeine	1163	194	
26	trichloro N-compund	1232	223	N
27	phenyl-9H-fluorene	1267	242	
28	ui tetrachloro N-compound	1425	257	N
29	ui	1529	237	N
30	dimethoxy phenanthrene	1634	238	
31	diphenyl pyridine	1793	231	

Table VI (cont'd)

no.	compound	scan number	MW	MS method
32	ui	1767	255	P
33	9-phenylphenanthrene	1875	254	
34	phenyl naphth[2,3-6]aze-2[H]one	1929	245	
35	trimethyl-diphenyl pyridinone	1966	289	
36	dioctyl phthalate	1945	390	
aliphatic hydrocarbons				
37	C ₁₅ H ₃₂		212	FID
38	C ₁₆ H ₃₄		226	FID
39	C ₁₈ H ₃₈		254	FID
40	C ₁₉ H ₄₀		268	FID
41	C ₂₀ H ₄₂		282	FID
42	C ₂₂ H ₄₆		310	FID
43	C ₂₄ H ₅₀		338	FID
44	C ₂₆ H ₅₄		366	FID
45	C ₂₇ H ₅₆		380	FID
46	C ₂₈ H ₅₈		394	FID
47	C ₂₉ H ₆₀		408	FID
48	C ₃₀ H ₆₂		422	FID
49	C ₃₁ H ₆₄		436	FID
50	C ₃₂ H ₆₆		450	FID
51	C ₃₃ H ₆₈		464	FID
52	C ₃₄ H ₇₀		478	FID
53	C ₃₅ H ₇₂		492	FID
54	C ₃₆ H ₇₄		506	FID

note: see Table IV

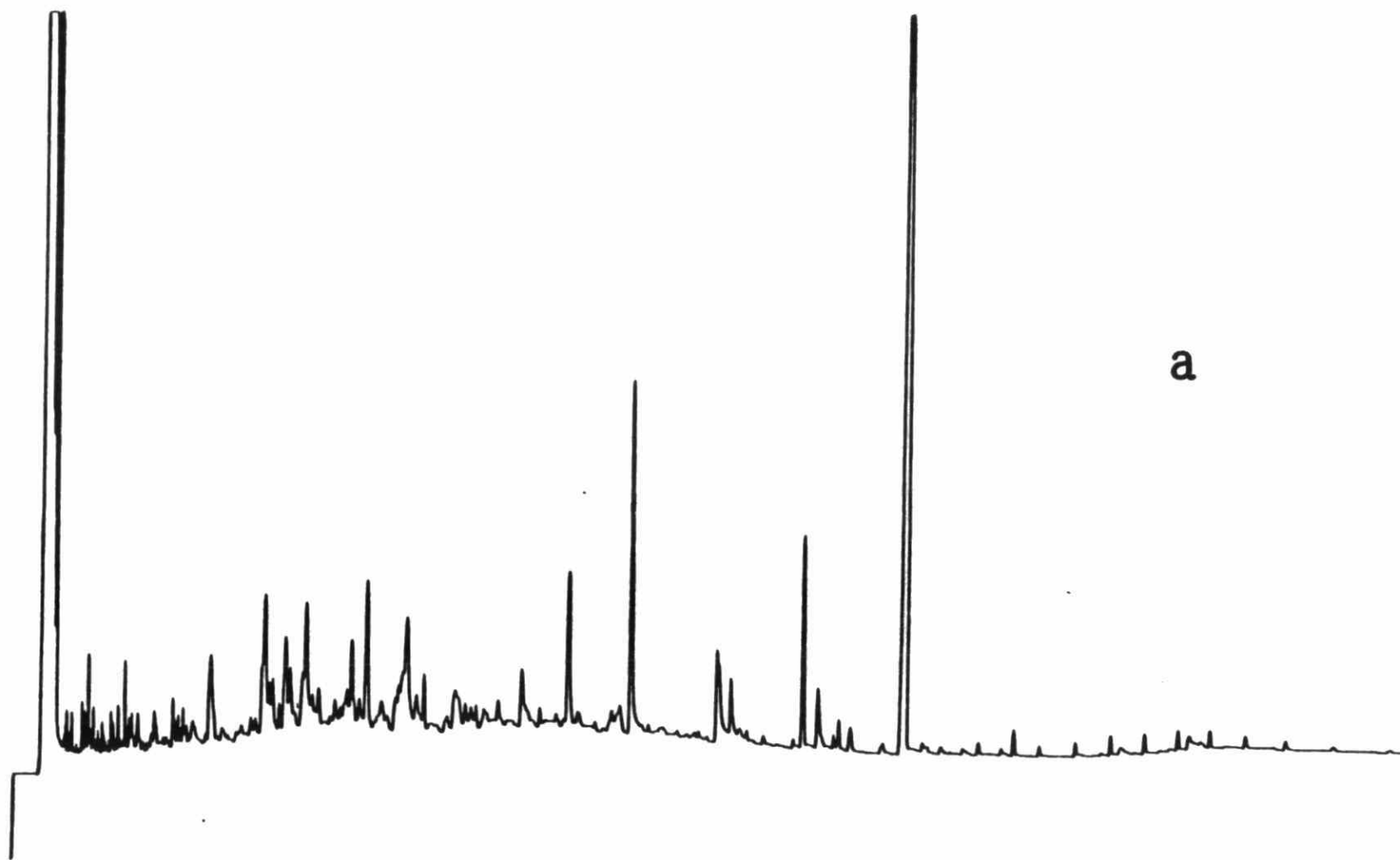


Figure 9: GC/FID traces of water extracts obtained at
(a) pH 4, (b) pH 7, and (c) pH 10

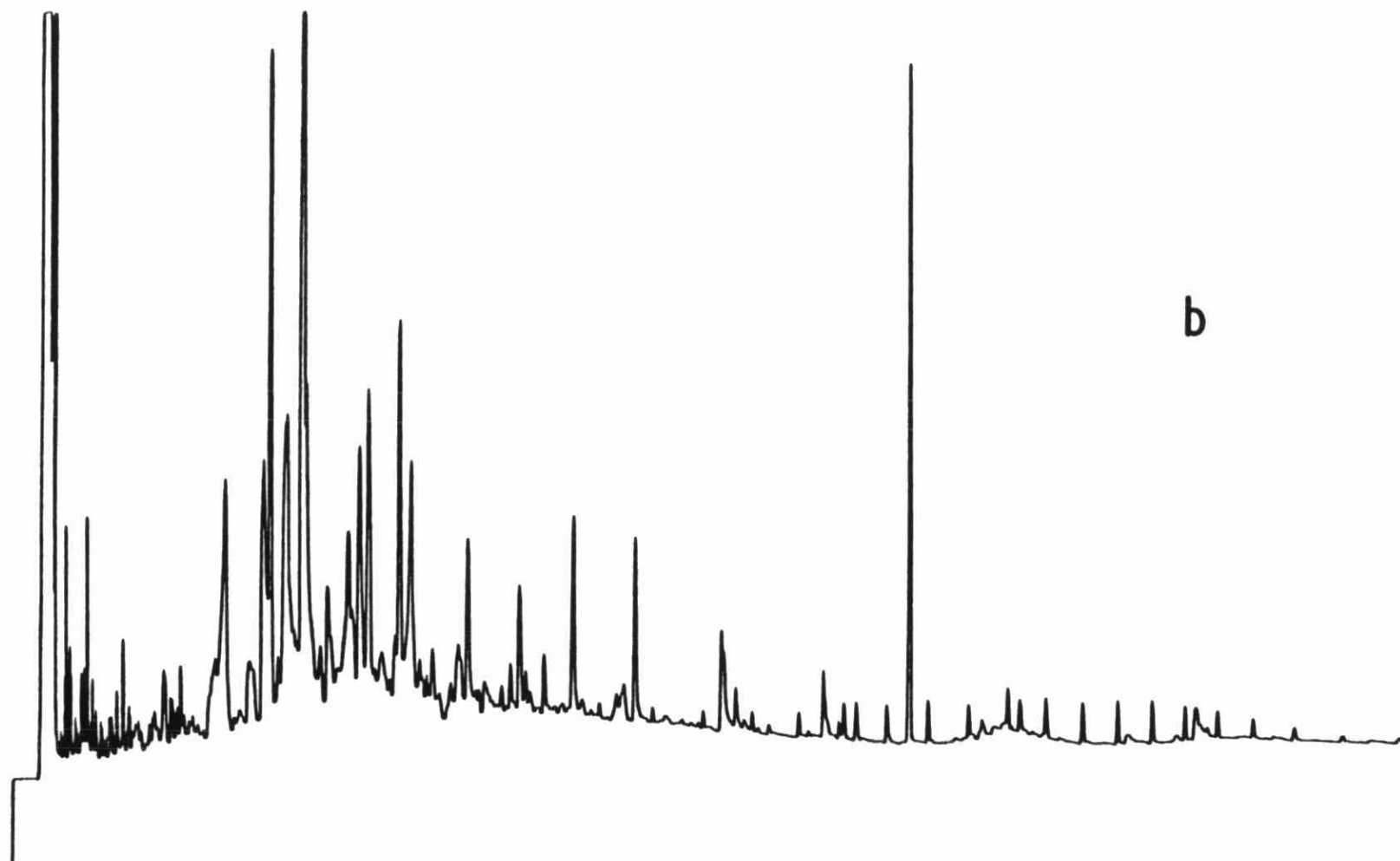


Figure 9 (continued)

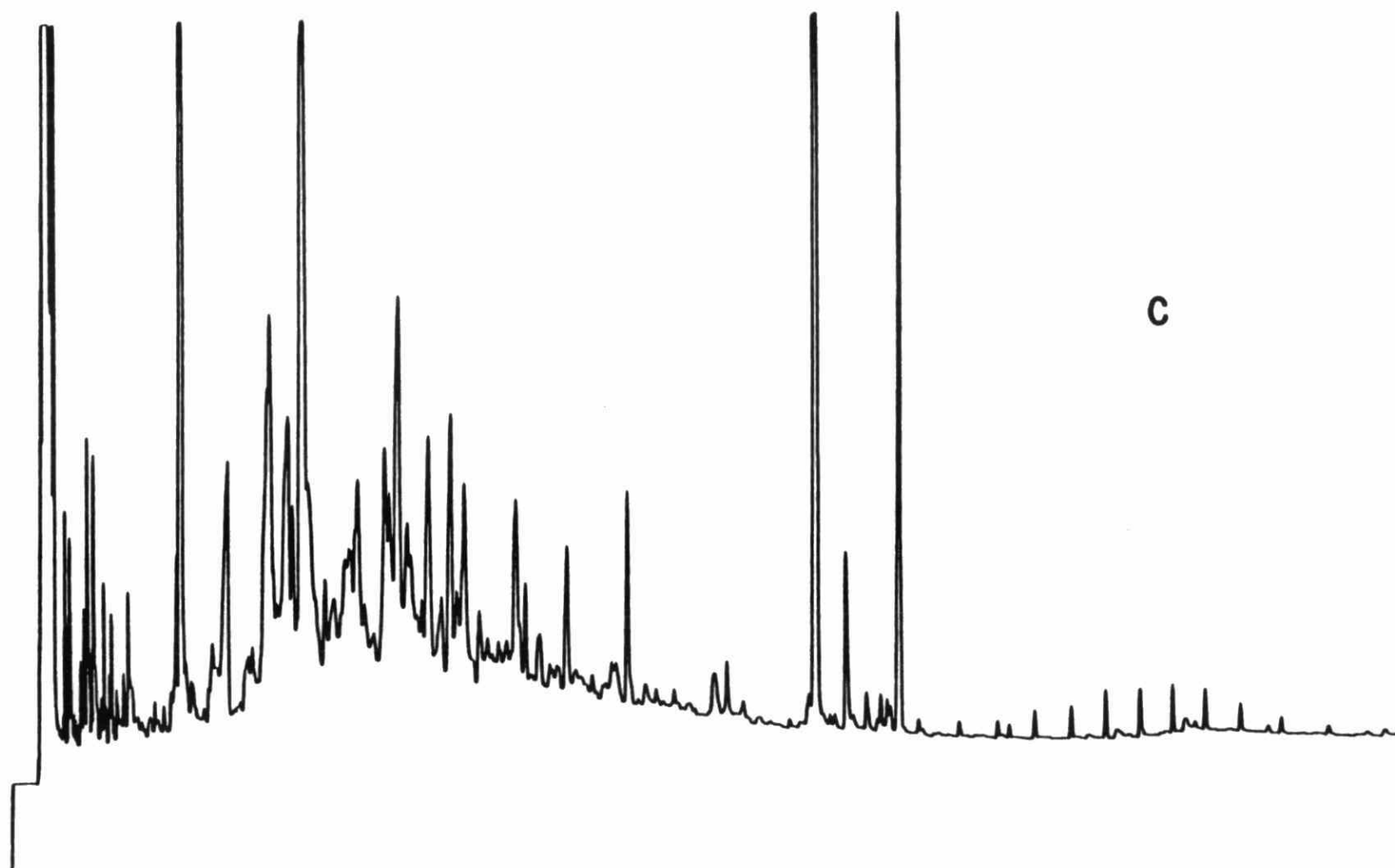


Figure 9 (continued)

gen-containing compounds and hydroxy-containing compounds were more prevalent in the extracts of pH 4 compared with those of pH 7. In the extract of pH 7, more polycyclic aromatic hydrocarbons were found.

Three Soxhlet extractions of water blanks were performed at the corresponding pH conditions. The GC/FID chromatograms of these three water blanks are shown in Figure 10. The organic compounds found in these water extraction blanks were not incorporated in the list of compounds identified in the flyash sample extracts.

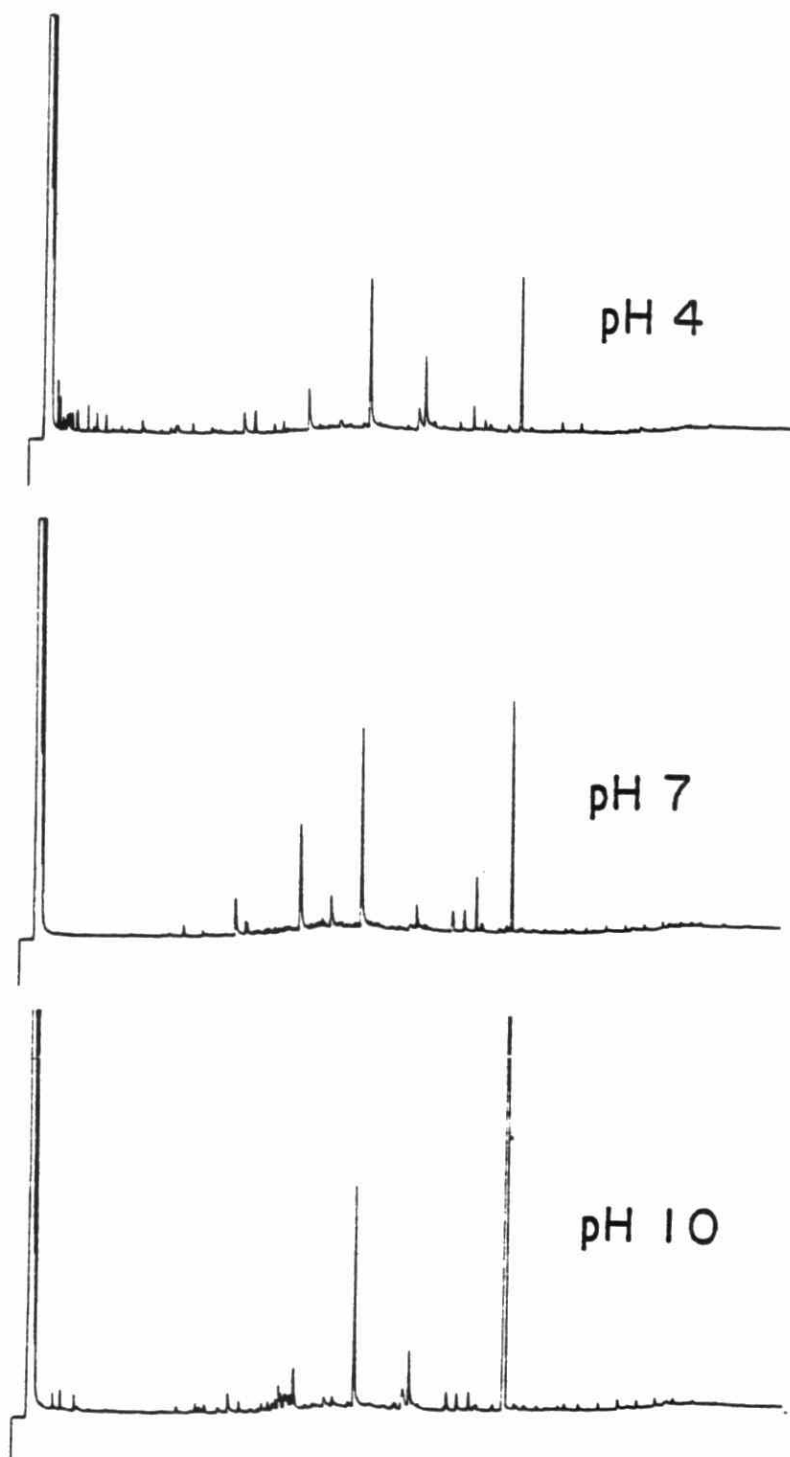


Figure 10: GC/FID chromatograms of extraction blanks

References

1. Rubel, F.N., "Incineration of Solid Waste", Pollution Technology Review No. 13, Noges Data Corp., Part Ridge, N.J., 1974: p. 56.
2. Tong, H.Y., Shore, D.L., and Karasek, F.W., "Identification of Organic Compounds Obtained from Incineration of Municipal Waste by High-Performance Liquid Chromatographic Fractionation and Gas Chromatography-Mass Spectrometry", 285 (1984) 423-441.
3. I.W. Davis, R.M. Harrison, R. Perry, D. Ratnayaka, and R.A. Wellings, Environ. Sci. Technol., 10, 451 (1976).
4. F.W. Karasek and F.I. Onuska, Anal. Chem., 54 (1982) 309A.
5. Tong, H.Y., Thompson, T.S., and Karasek, F.W., "Multiple Confirmation of GC/MS Identification", accepted for presentation at the 33rd American Society of Mass Spectrometry, San Diego, CA., May 26, 1985.

Appendix
Mass Spectra Data of Unidentified Compounds
in Water Extract Samples

Captions

LF-4 - water extract of pH 4

LF-7 - water extract of pH 7

LF-10 - water extract of pH 10

scan - MS scan number, corresponding to Table IV, V, and VI

PCILIN - mass spectra obtained at linear scan mode of GC/PICIMS

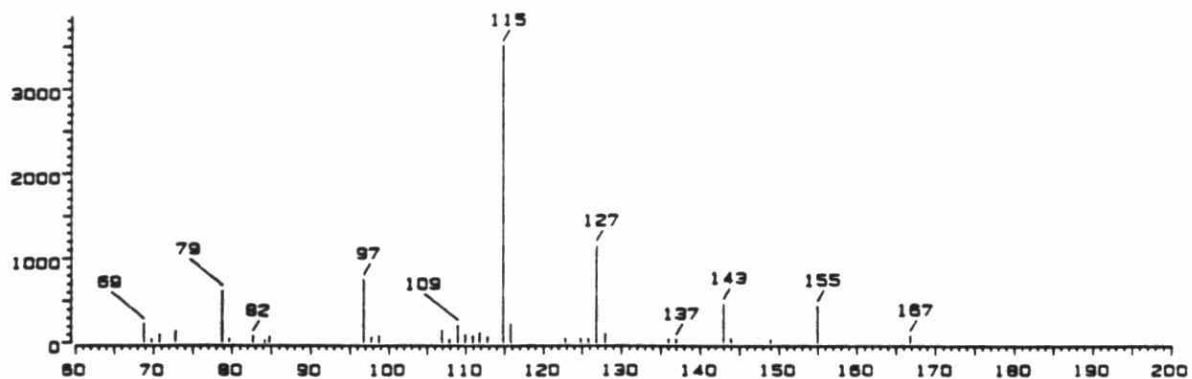
NCILIN - mass spectra obtained at linear scan mode of GC/NICIMS

File >Y1489
8pk Ab 3501

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 21
5.47 min.

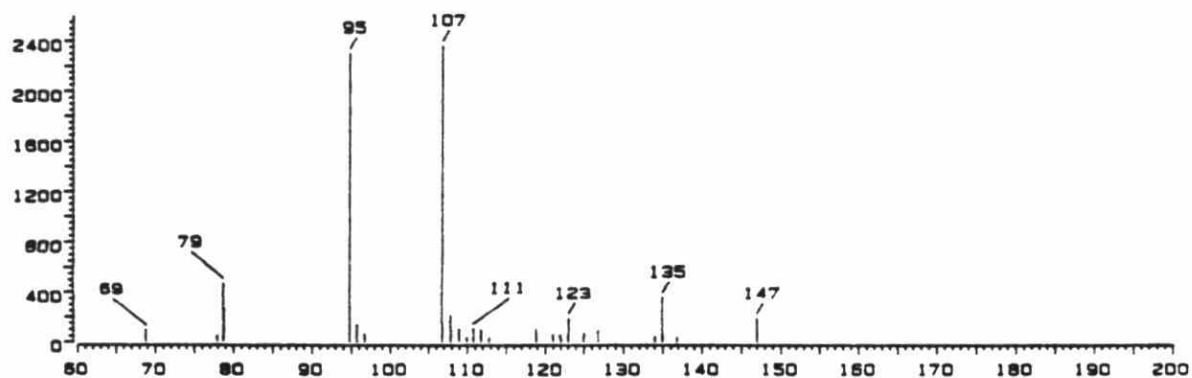


File >Y1489
8pk Ab 2359

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 34
5.67 min.

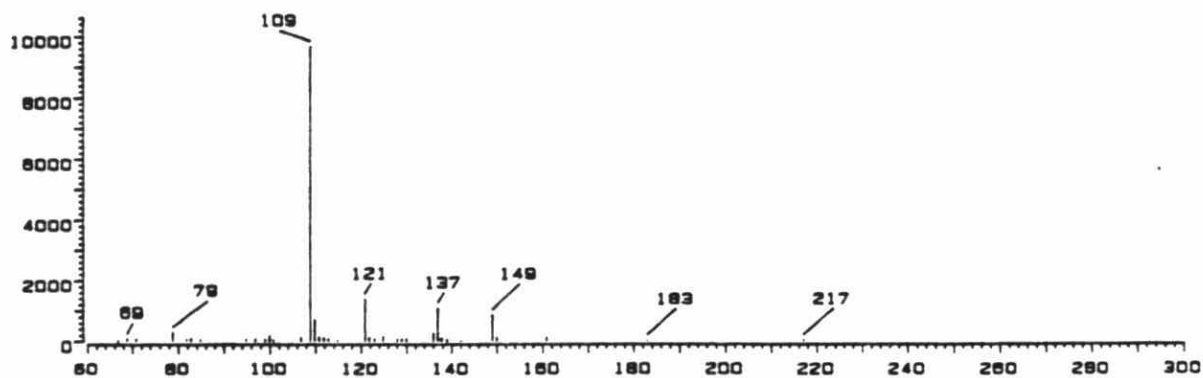


File >Y1489
8pk Ab 9684

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 58
6.02 min.

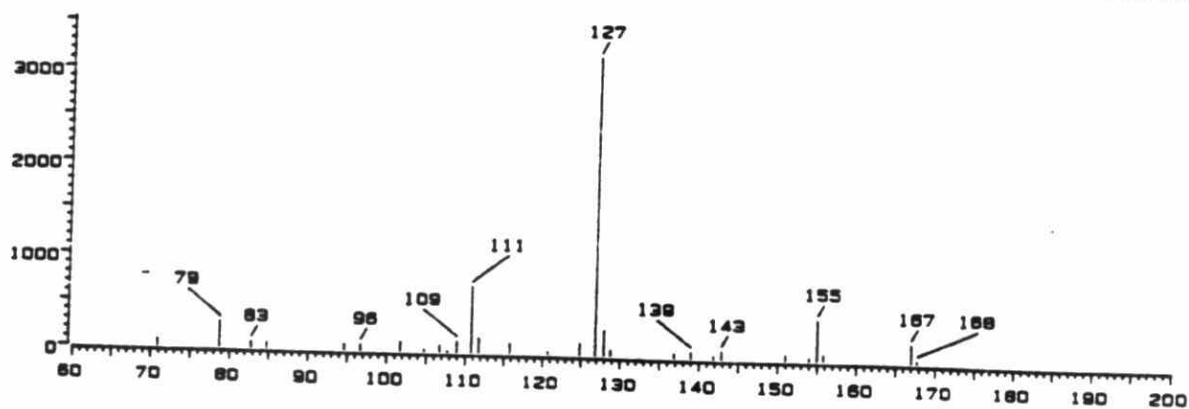


File >Y1489
Sph Ab 3205

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 75
6.32 min.

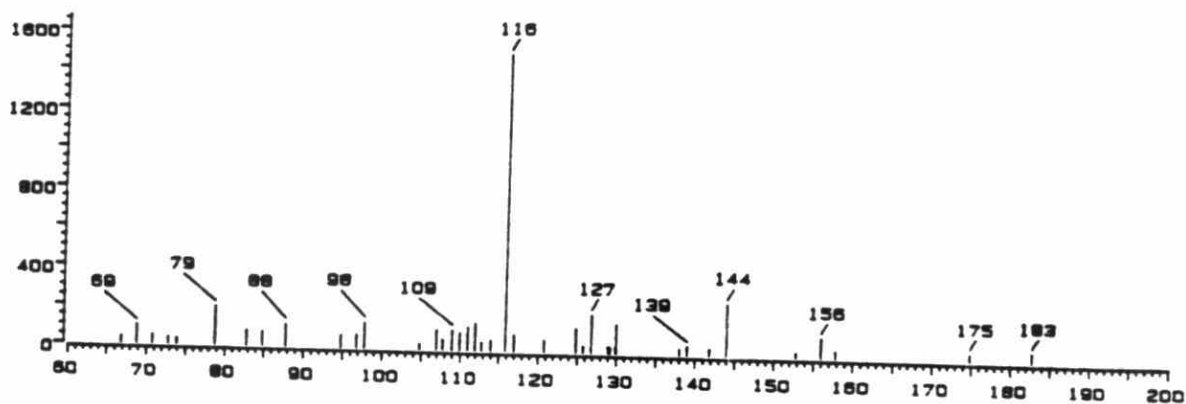


File >Y1489
Sph Ab 1513

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 111
6.89 min.

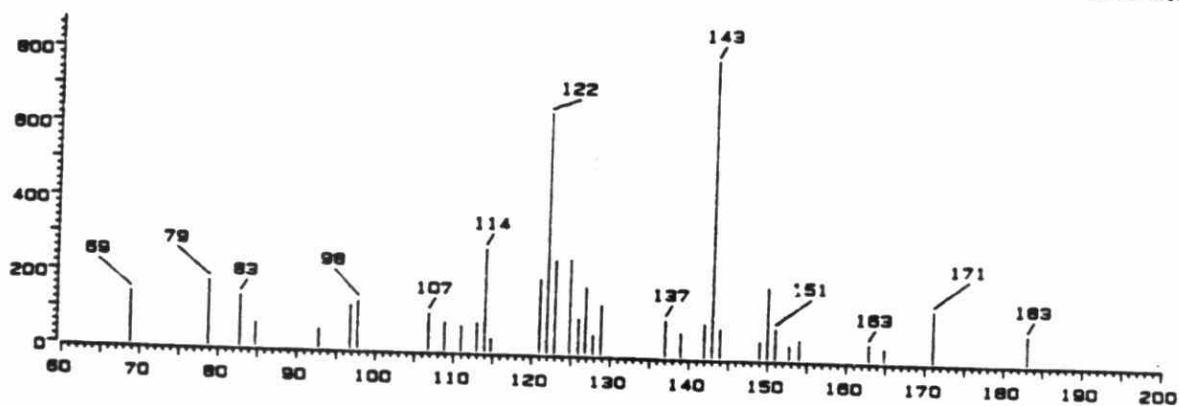


File >Y1489
Sph Ab 797

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 172
7.88 min.

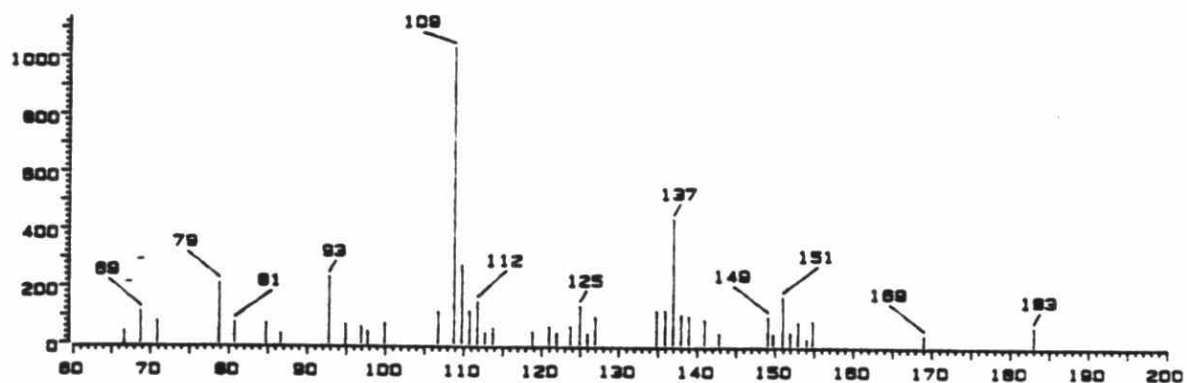


File >Y1489
Sph Ab 1032

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 208
8.40 min.

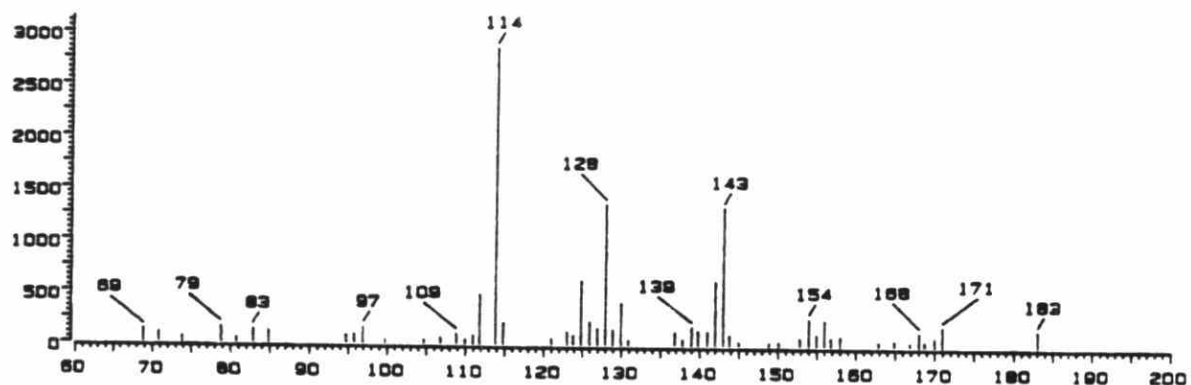


File >Y1489
Sph Ab 2853

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 311
10.07 min.

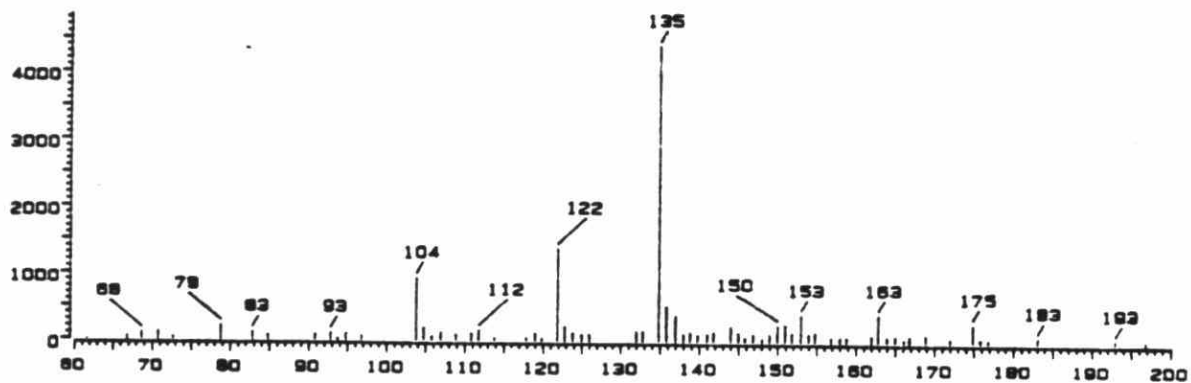


File >Y1489
Sph Ab 4404

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 459
12.42 min.

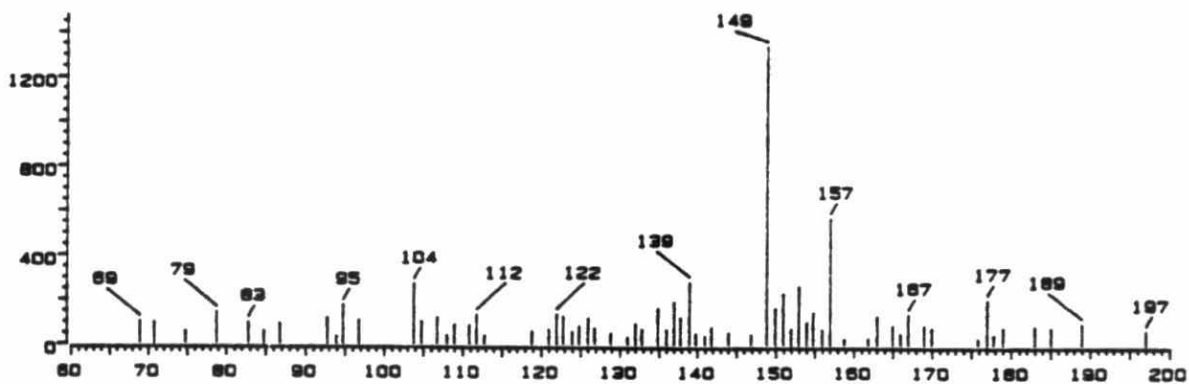


File >Y1488
Spk Ab 1342

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 483
12.80 min.

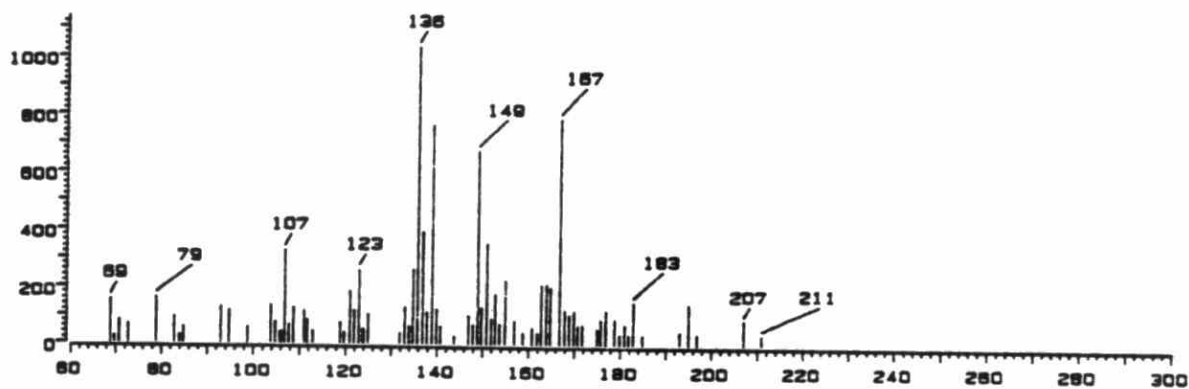


File >Y1488
Spk Ab 1033

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 508
13.20 min.

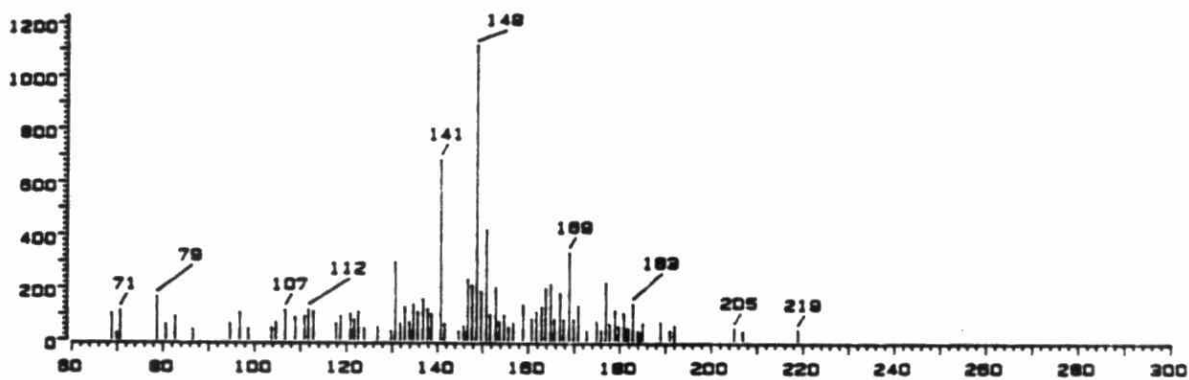


File >Y1488
Spk Ab 1118

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 651
15.47 min.

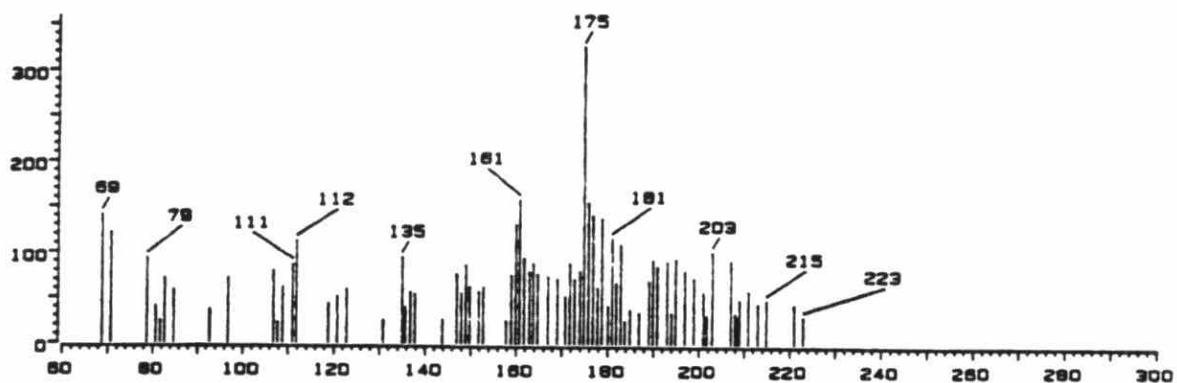


File >Y1489
Spk Ab 326

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 958
20.37 min.

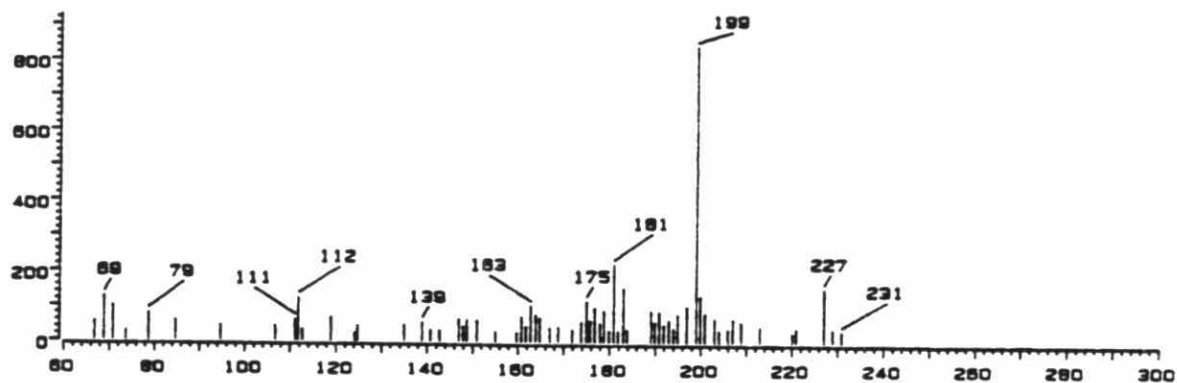


File >Y1489
Spk Ab 842

LF-4-4-7

LF-4-4-7 (20uL) PCILIN

Scan 1038
21.63 min.

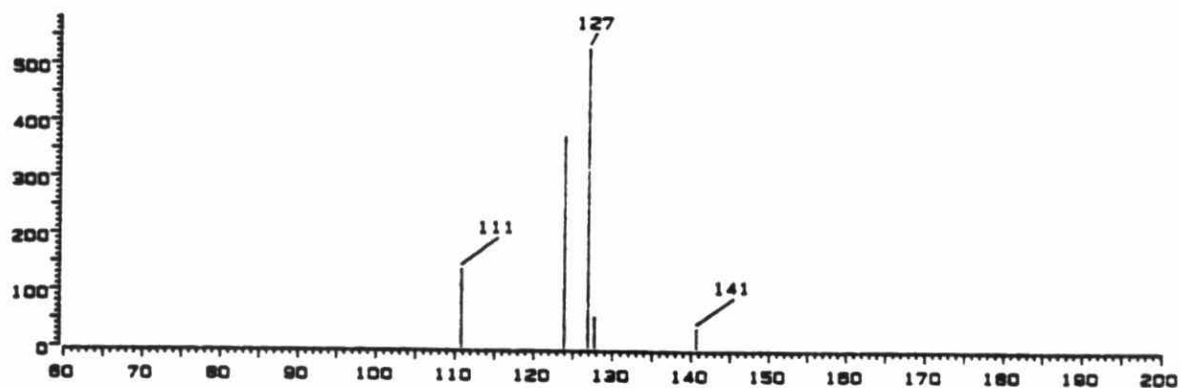


File >Y1499
Spk Ab 529

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 123
7.24 min.

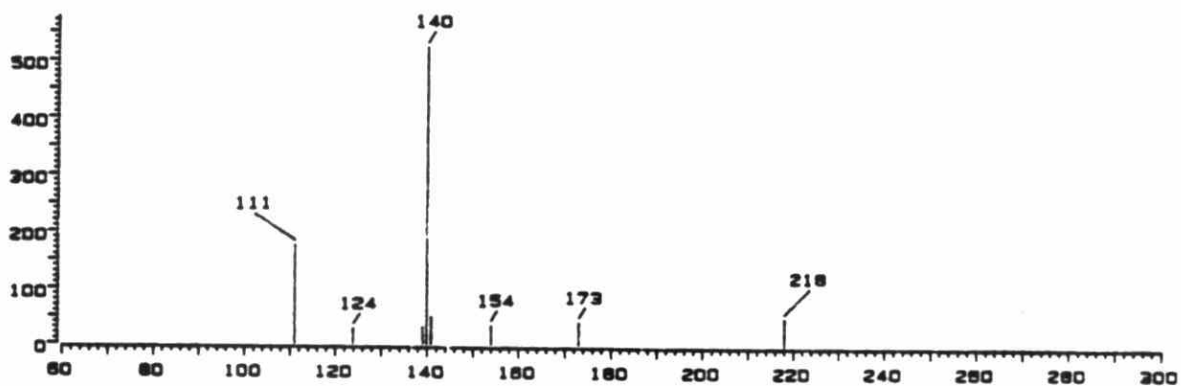


File >Y1499
Spk Ab 529

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 259
9.22 min.

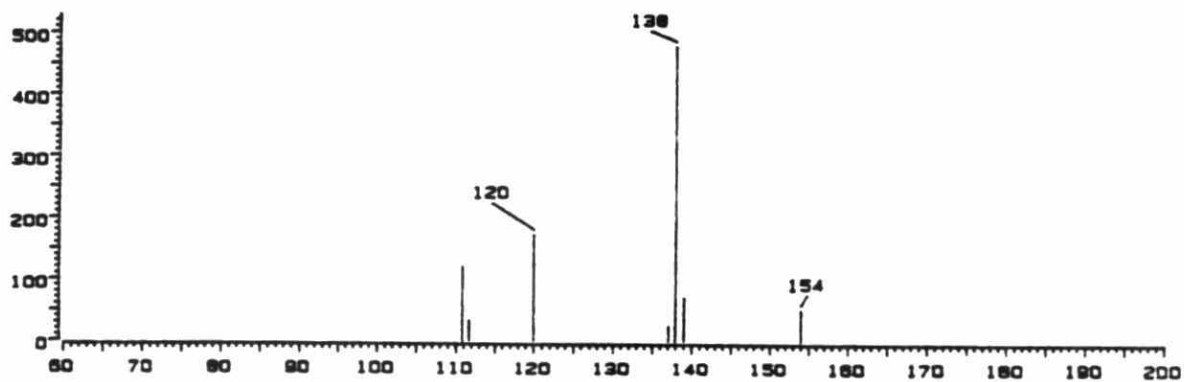


File >Y1499
Spk Ab 480

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 284
9.53 min.

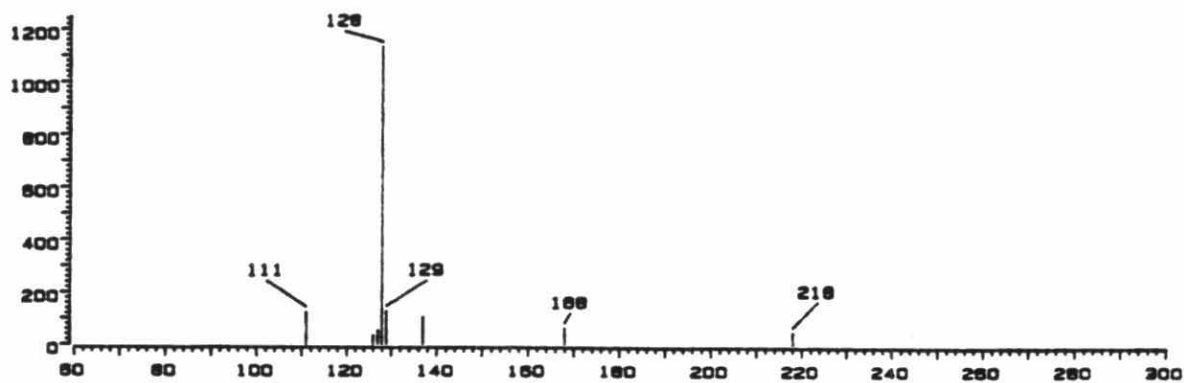


File >Y1499
Spk Ab 1124

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 421
11.80 min.

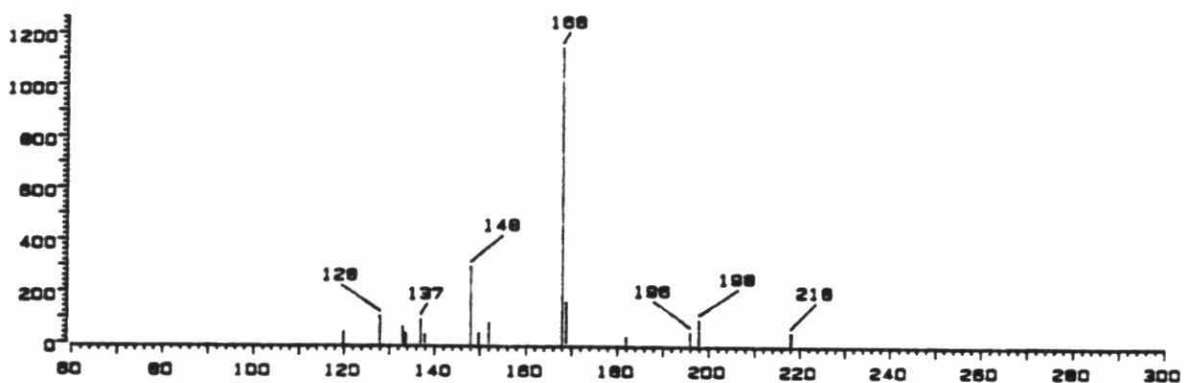


File >Y1499
Spk Ab 1145

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 433
11.99 min.

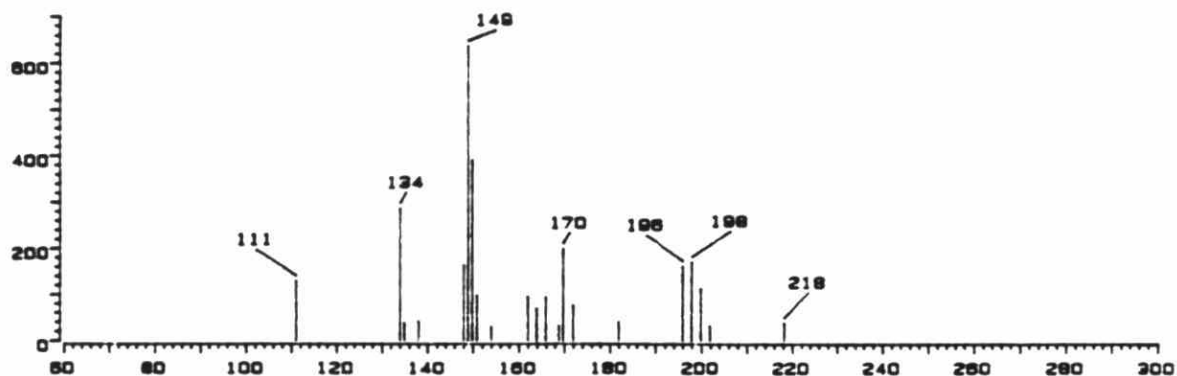


File >Y1499
Spk Ab 527

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 535
12.60 min.

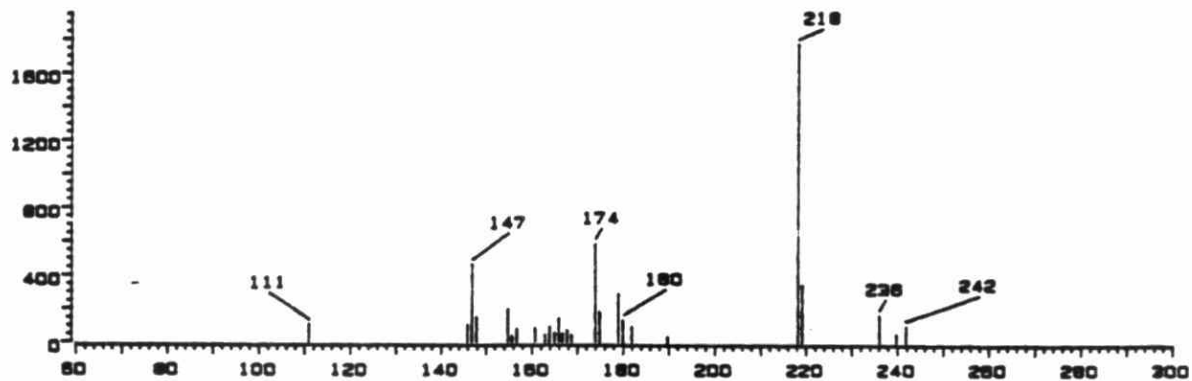


File >Y1499
Spk Ab 1779

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 849
15.41 min.

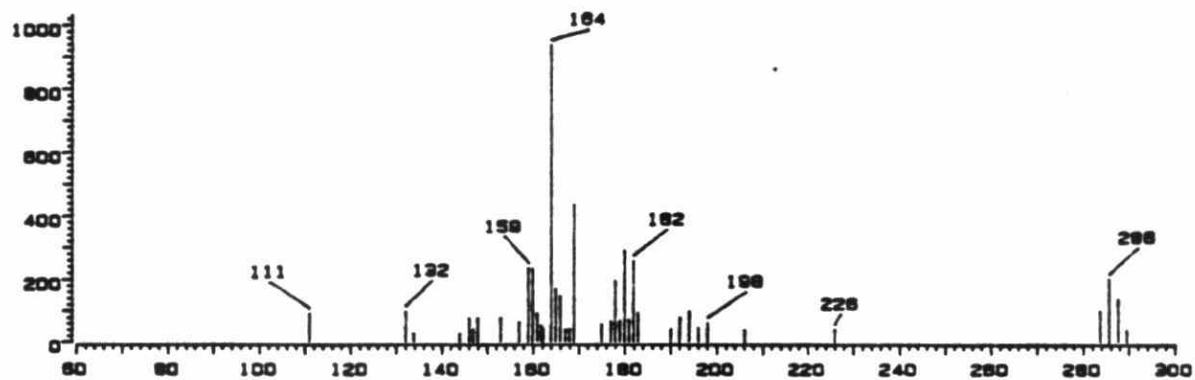


File >Y1499
Spk Ab 938

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 787
17.28 min.

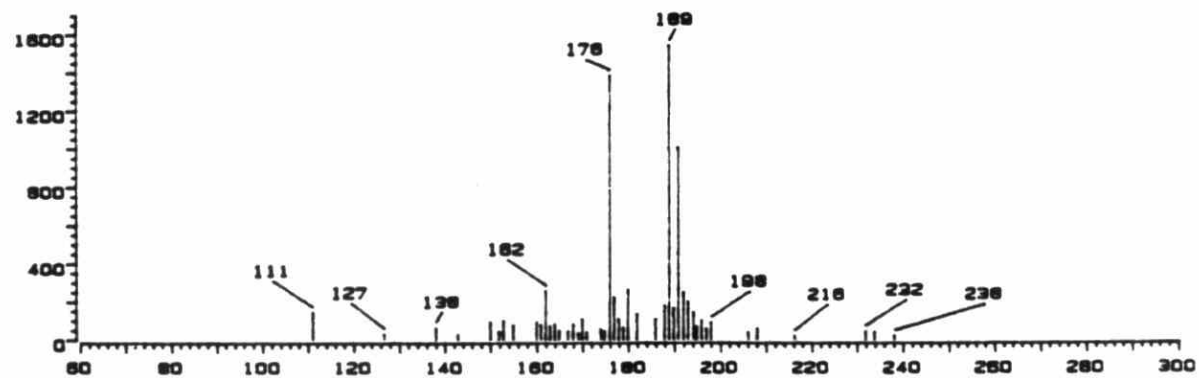


File >Y1499
Spk Ab 1544

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 887
18.87 min.

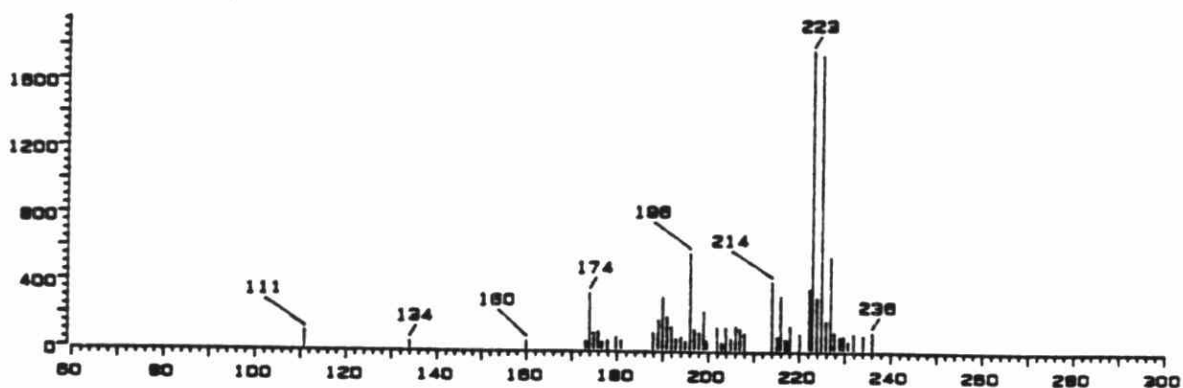


File >Y1488
Spk Ab 1783

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1134
23.11 min.

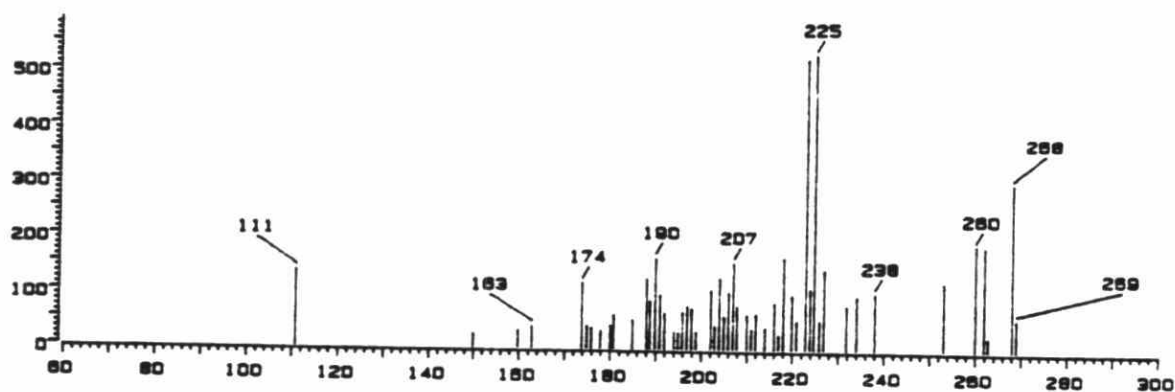


File >Y1488
Spk Ab 535

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1184
23.90 min.

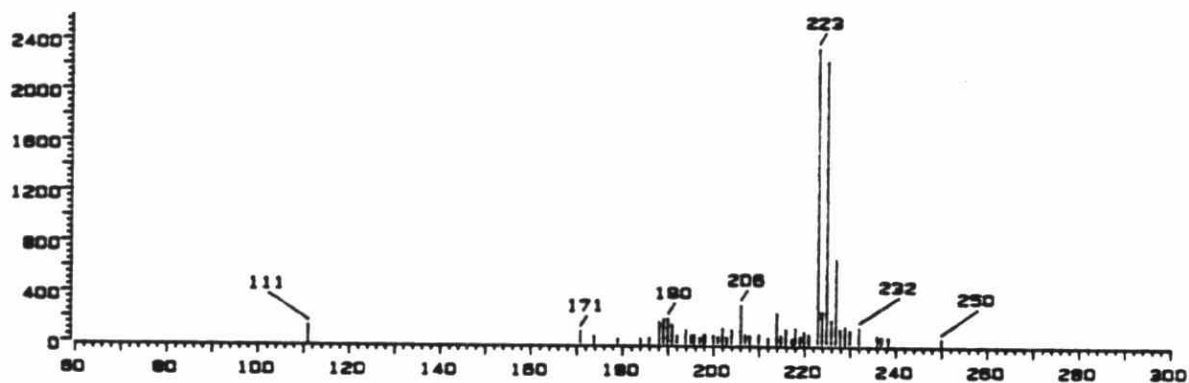


File >Y1488
Spk Ab 2345

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1215
24.38 min.

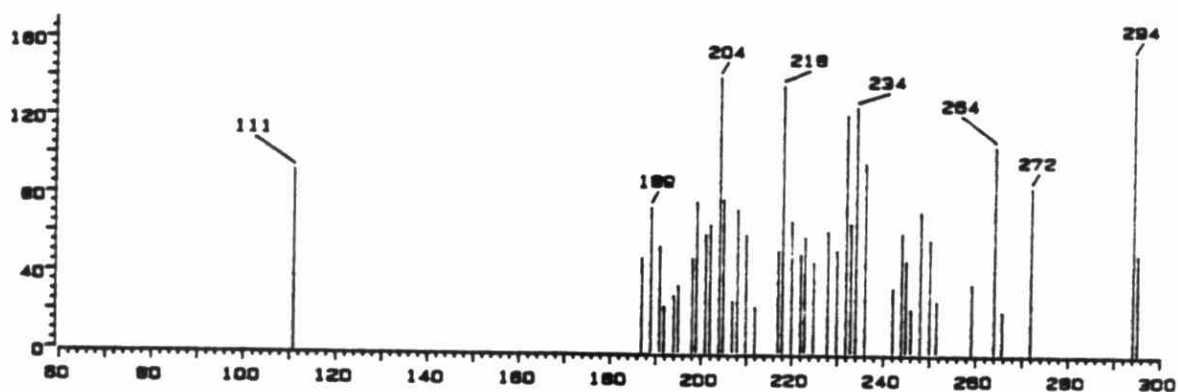


File >Y1488
Sph Ab 154

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1375
26.93 min.

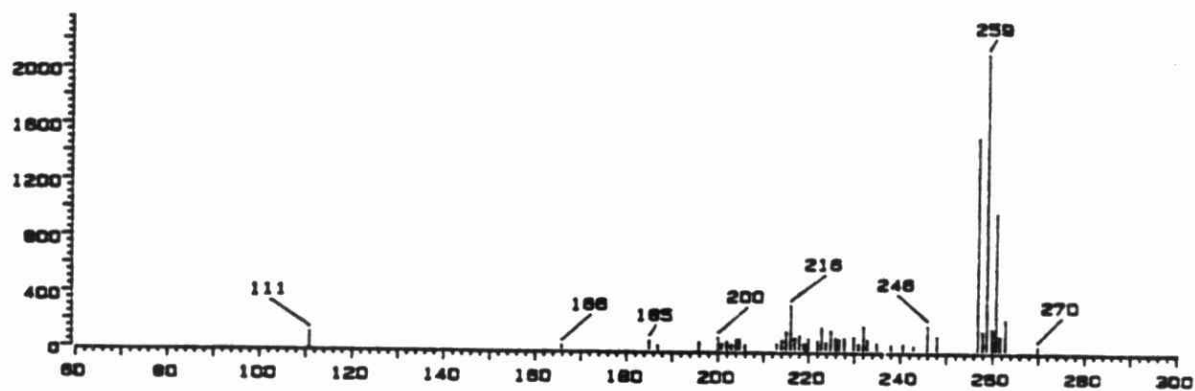


File >Y1488
Sph Ab 2134

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1422
27.88 min.

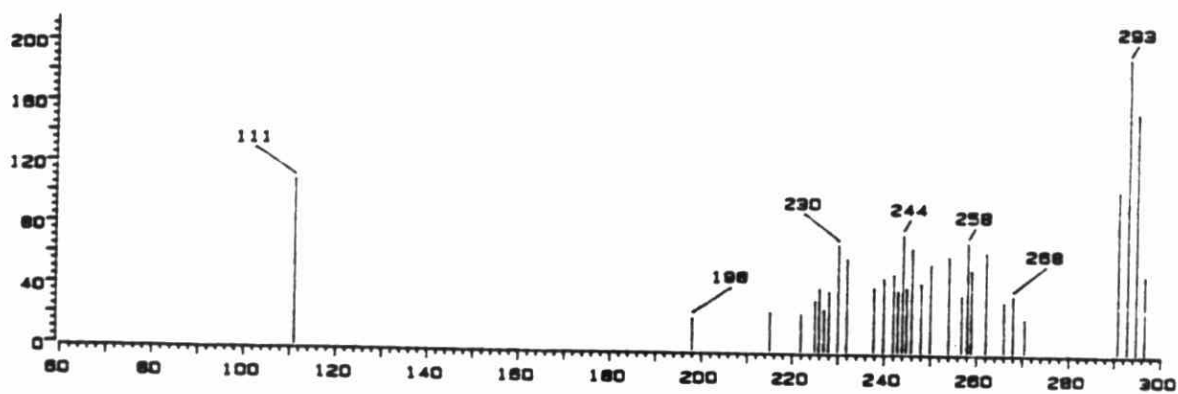


File >Y1488
Sph Ab 185

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1671
31.83 min.

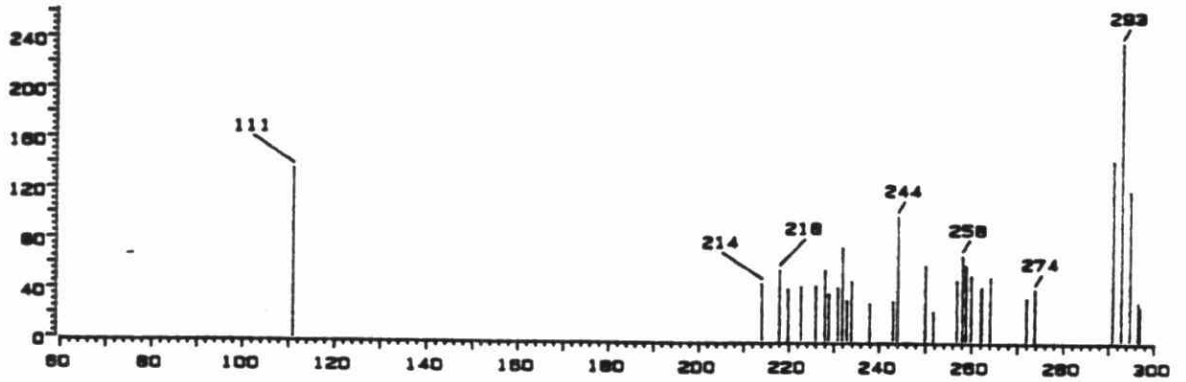


File >Y1499
Spk Ab 238

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1875
31.89 min.

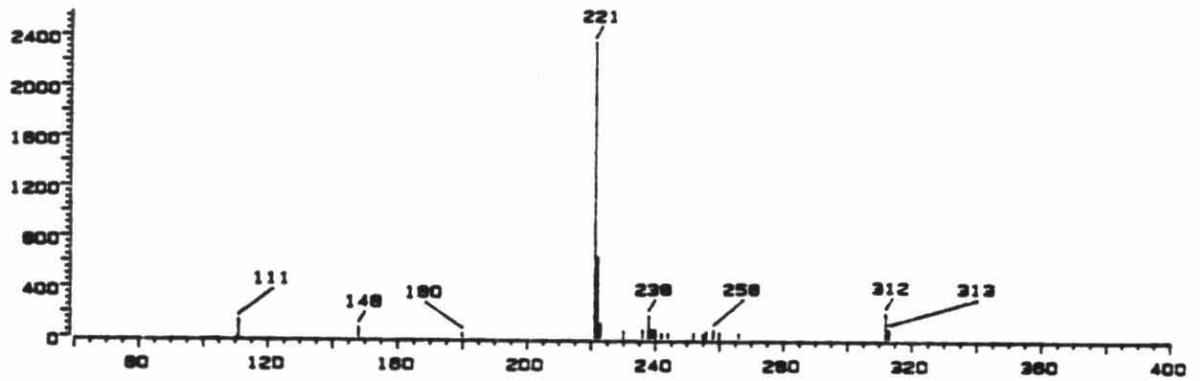


File >Y1499
Spk Ab 2347

LF-4-4-8

LF-4-4-8 (20uL) NCILIN

Scan 1798
33.85 min.

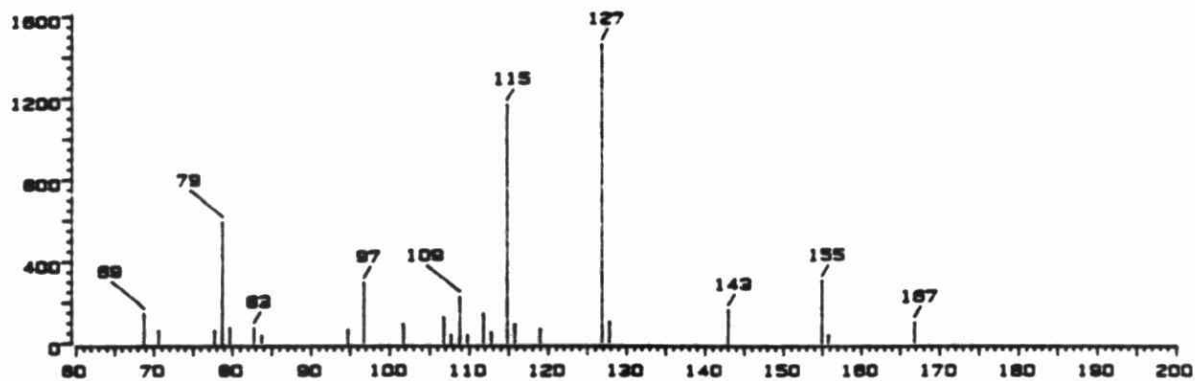


File >Y1488
Sph Ab 1453

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 21
5.47 min.

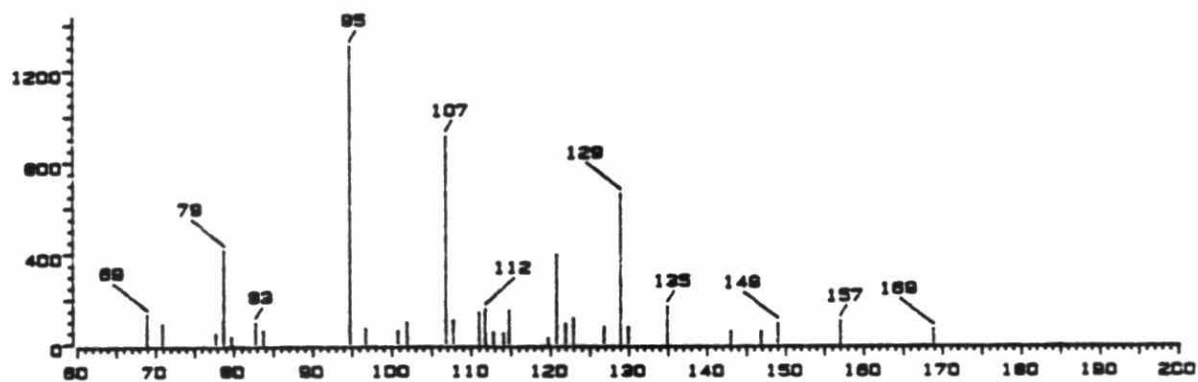


File >Y1488
Sph Ab 1203

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 37
5.72 min.

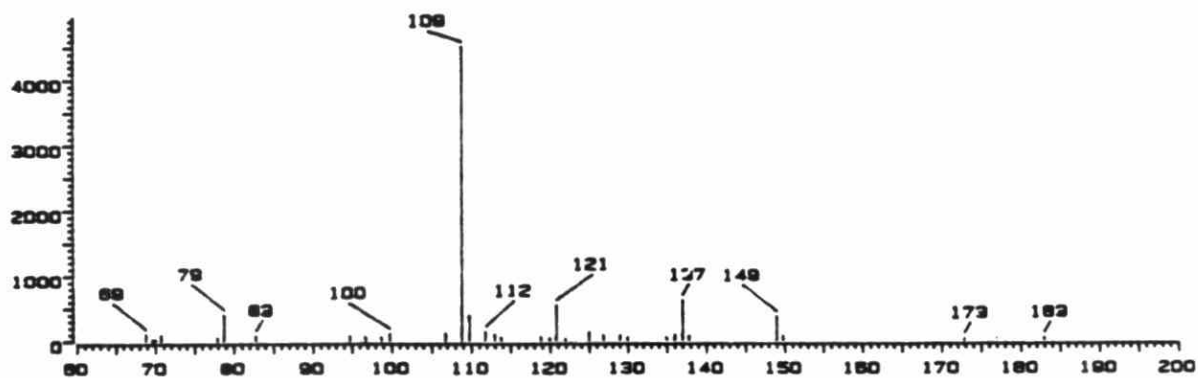


File >Y1488
Sph Ab 4506

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 57
6.04 min.

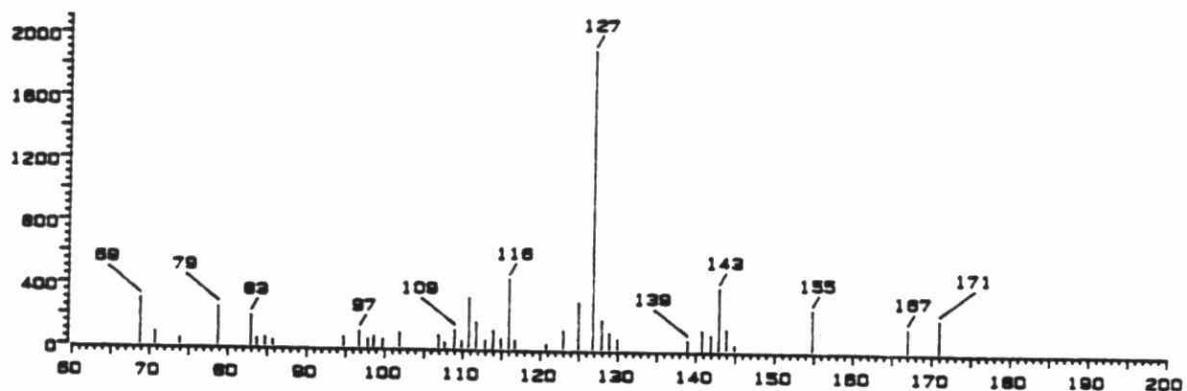


File >Y1488
Bpk Ab 1807

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 77
8.38 min.

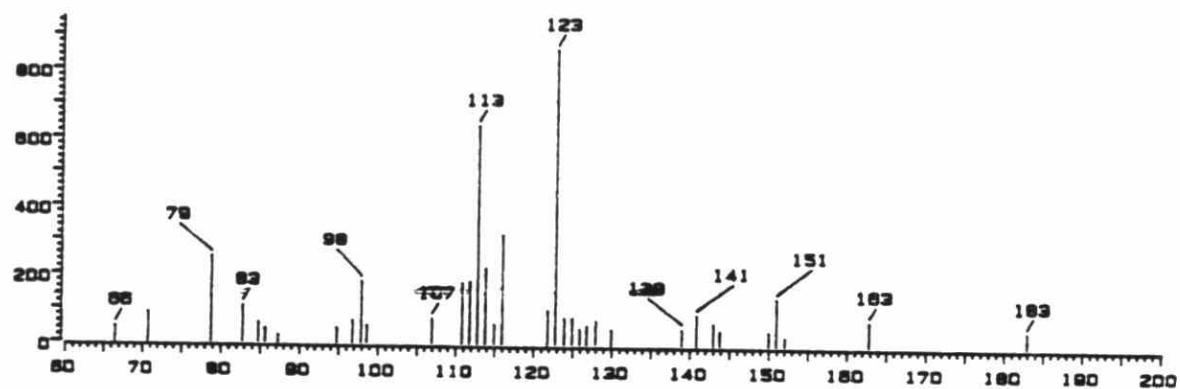


File >Y1488
Bpk Ab 863

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 93
8.61 min.

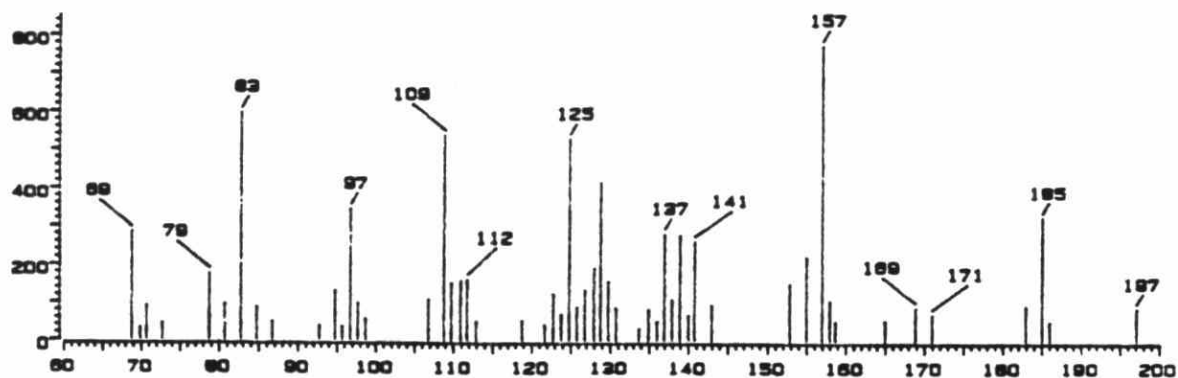


File >Y1488
Bpk Ab 774

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 224
8.88 min.

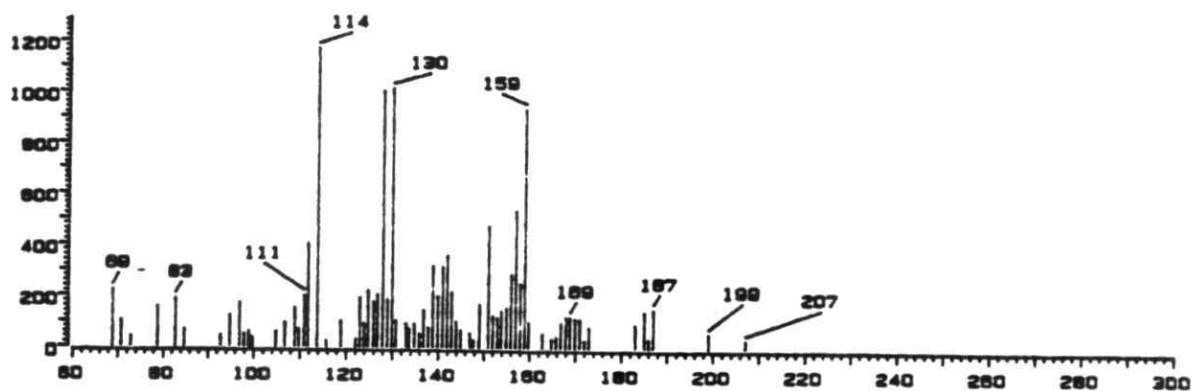


File >Y1488
Spk Ab 1170

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 341
10.55 min.

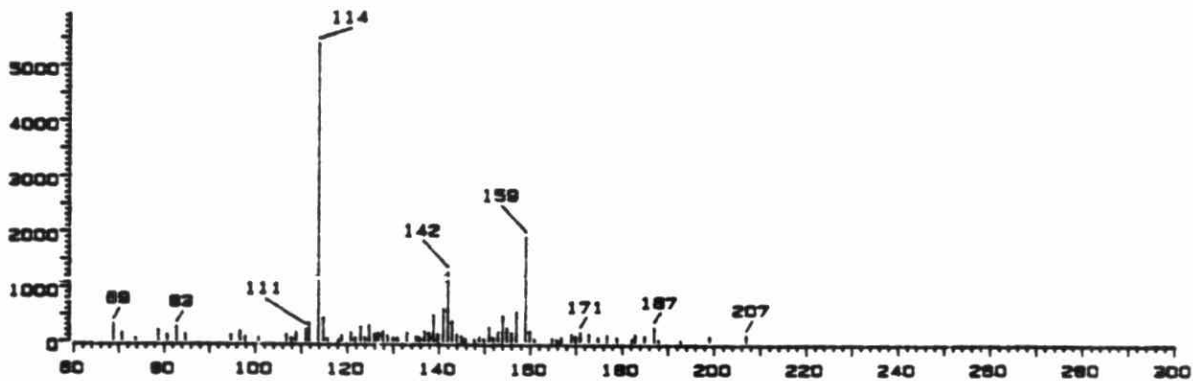


File >Y1488
Spk Ab 5394

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 366
10.95 min.

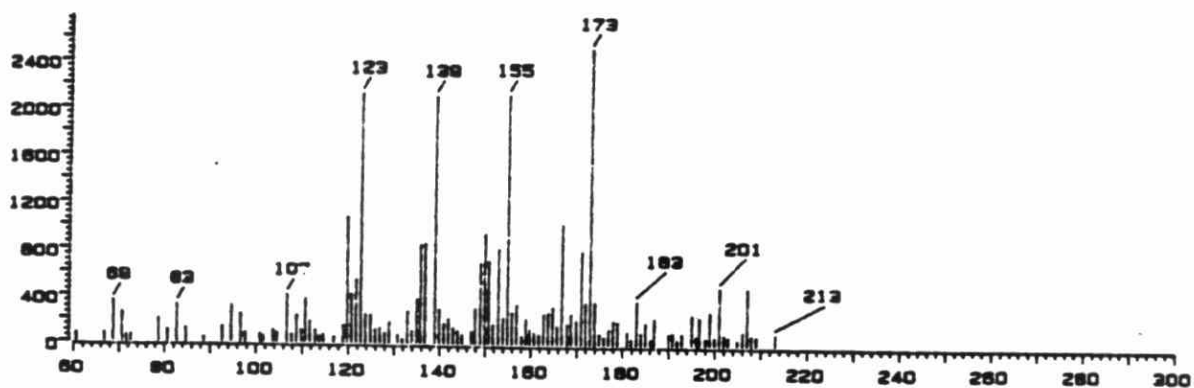


File >Y1488
Spk Ab 2517

LF-7-11-5

LF-7-11-5 (20uL) PCILIN

Scan 516
12.34 min.

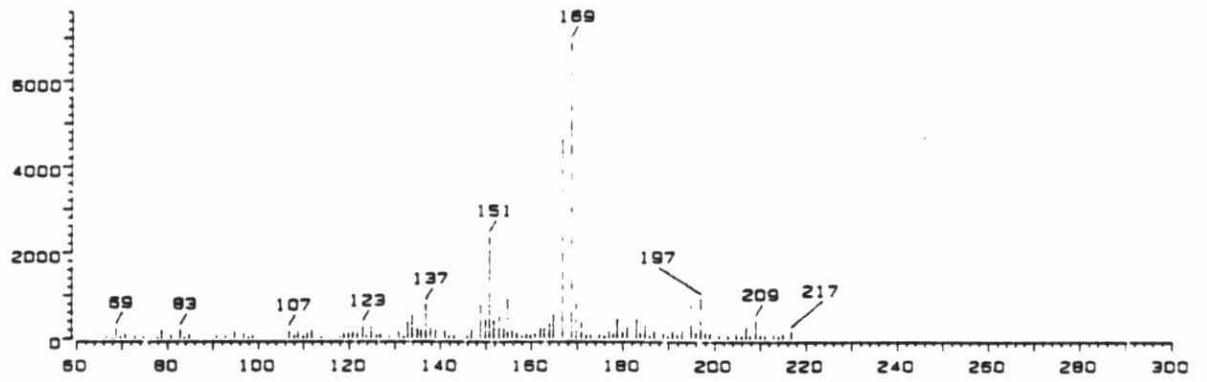


File >Y1488
Bpk Ab 6897

LF-7-11-5

LF-7-11-5 (20UL) PCILIN

Scan 677
15.91 min.

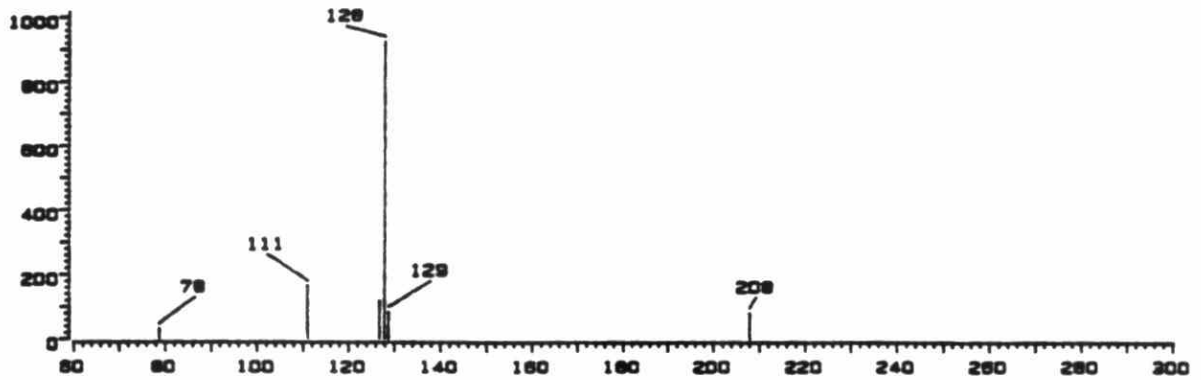


File >Y1496
Spk Ab 525

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 321
10.21 min.

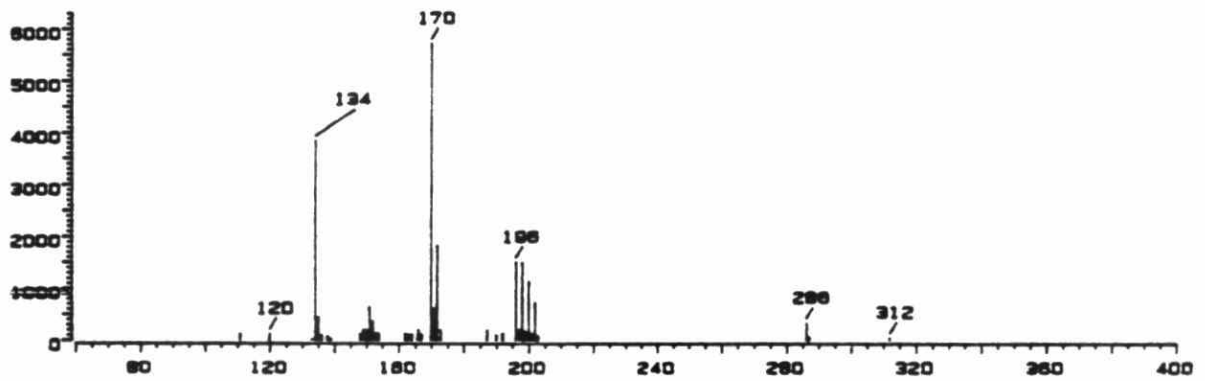


File >Y1496
Spk Ab 5721

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 539
13.67 min.

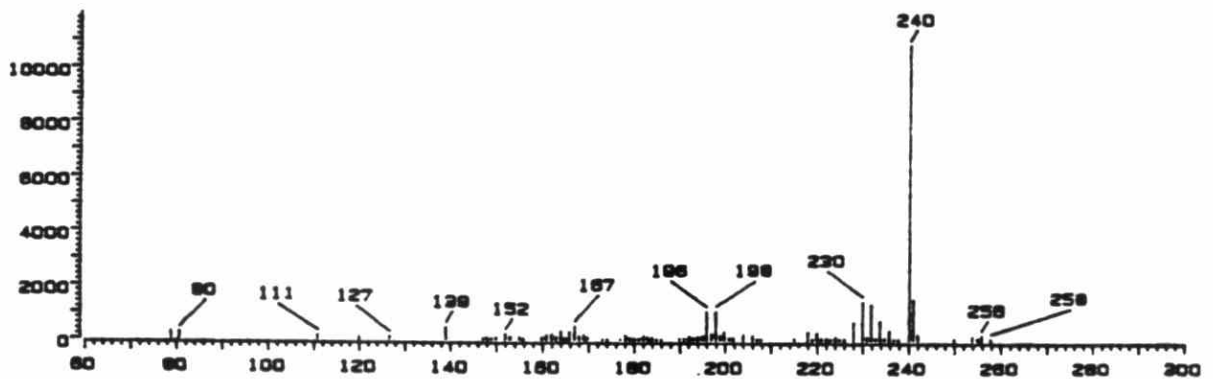


File >Y1496
Spk Ab 10678

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 815
16.05 min.

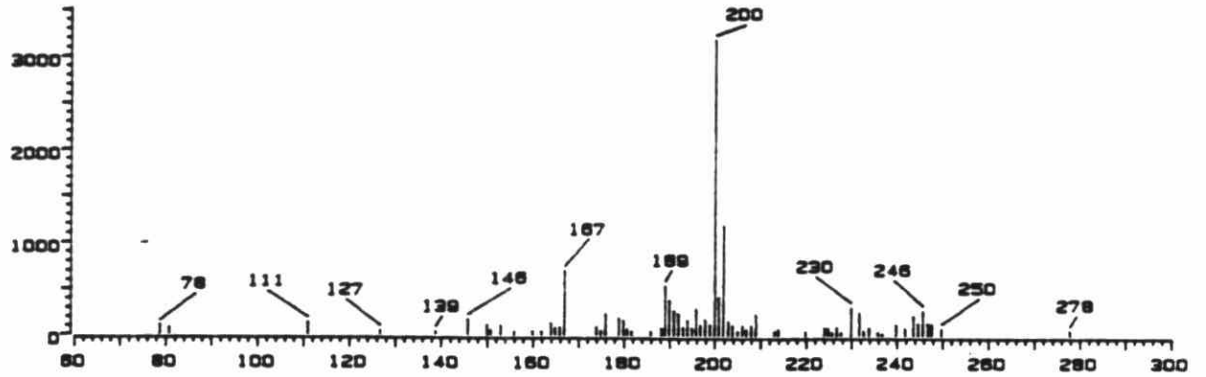


File >Y1496
Sph Ab 2195

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 986
20.77 min.

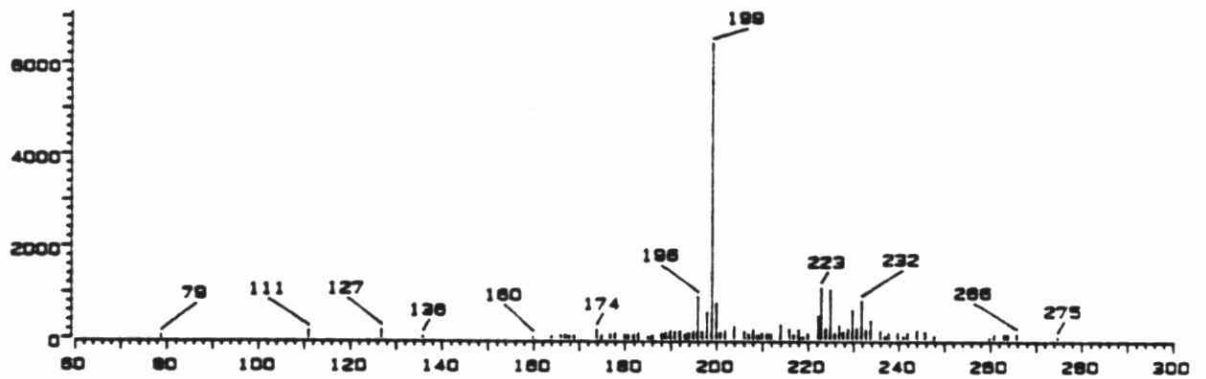


File >Y1496
Sph Ab 6429

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 1131
22.08 min.

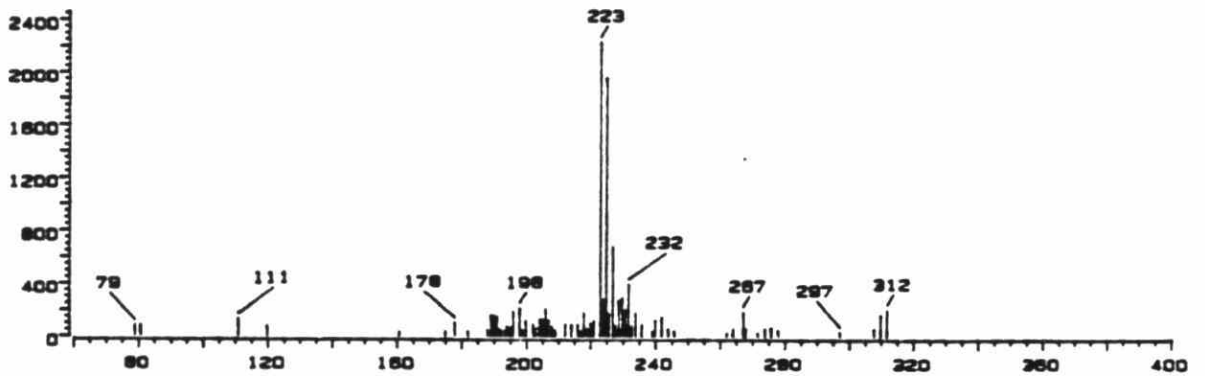


File >Y1496
Sph Ab 2237

LF-7-11-6

LF-7-11-6 (20uL) NCILIN

Scan 1219
24.48 min.

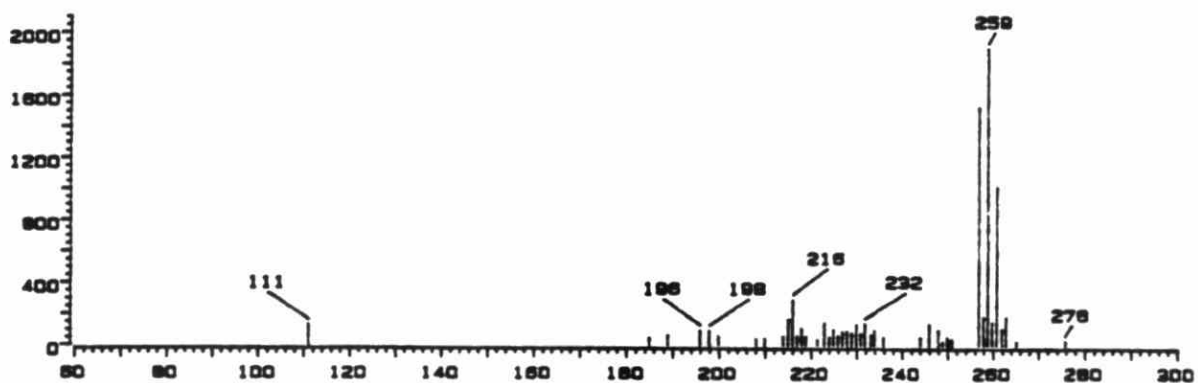


File >Y1498
Spk Ab 1808

LF-7-11-8

LF-7-11-8 (20uL) NCILIN

Scan 1423
27.72 min.

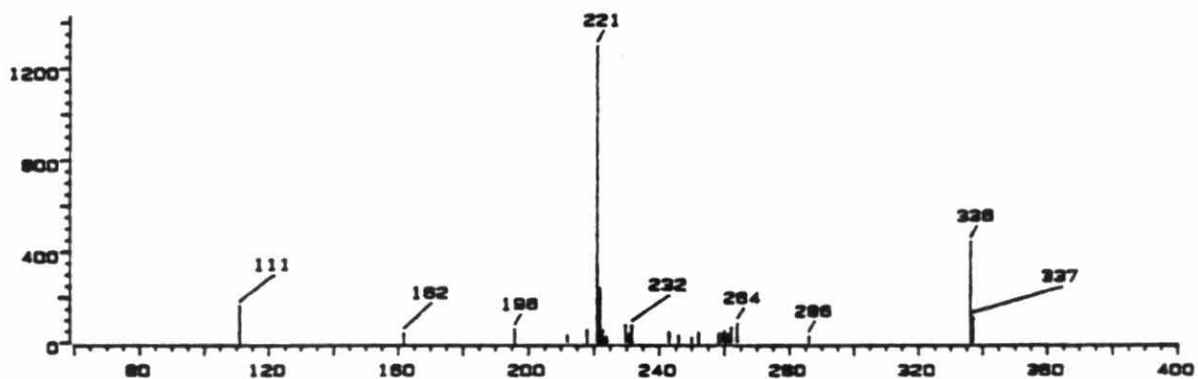


File >Y1498
Spk Ab 1298

LF-7-11-8

LF-7-11-8 (20uL) NCILIN

Scan 1758
33.00 min.

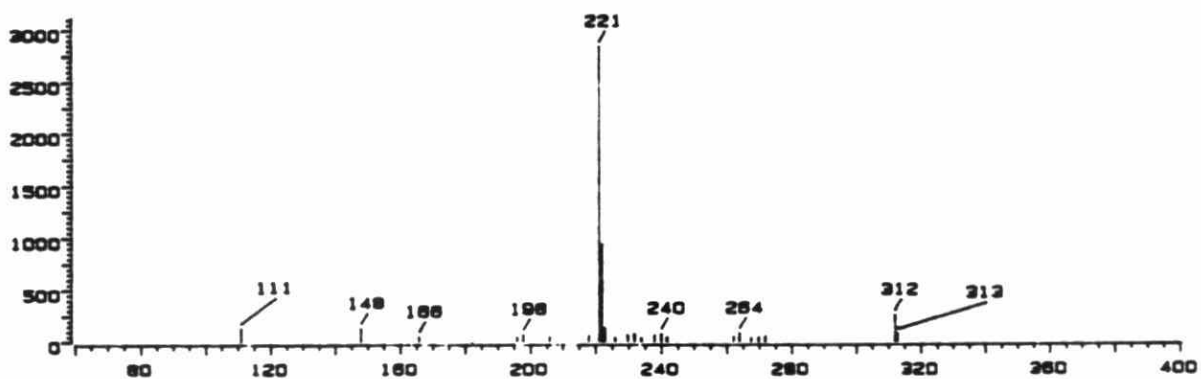


File >Y1498
Spk Ab 2833

LF-7-11-8

LF-7-11-8 (20uL) NCILIN

Scan 1798
33.67 min.

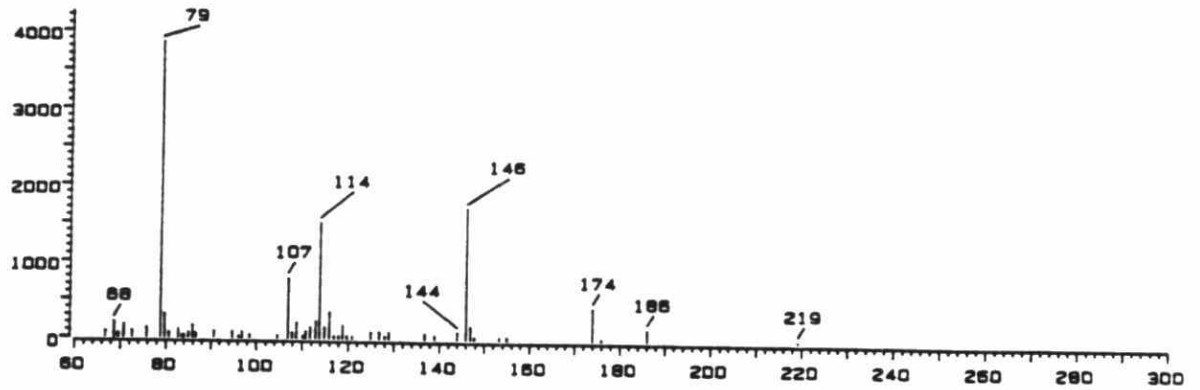


File >Y1745
8pk Ab 3852

LF-10-2

PCI

Scan 22
5.51 min.

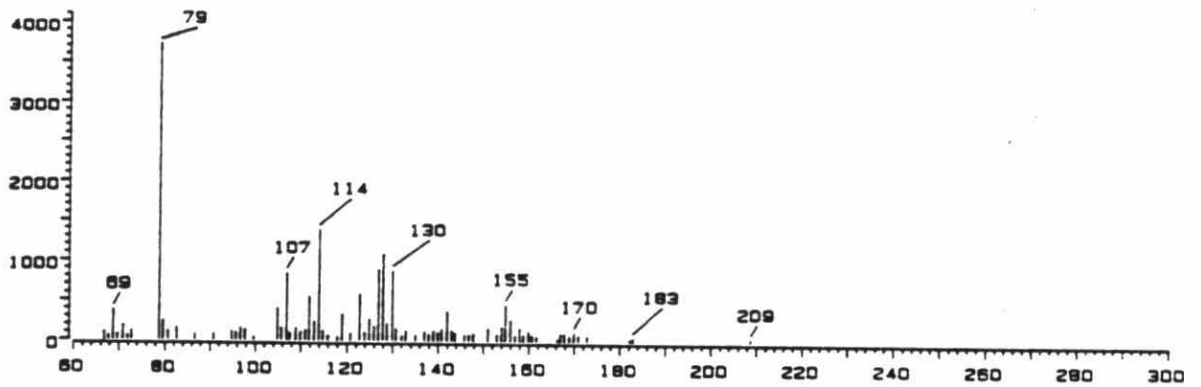


File >Y1745
8pk Ab 3723

LF-10-2

PCI

Scan 267
9.32 min.

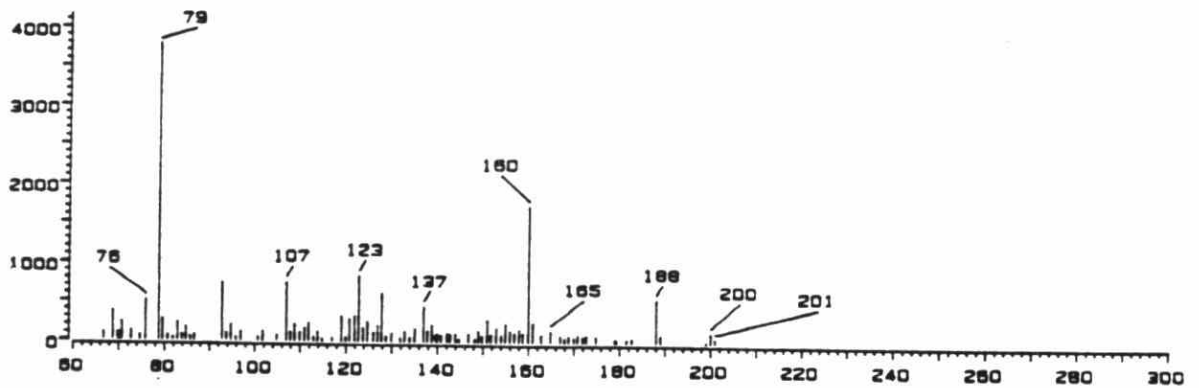


File >Y1745
8pk Ab 3782

LF-10-2

PCI

Scan 354
10.67 min.

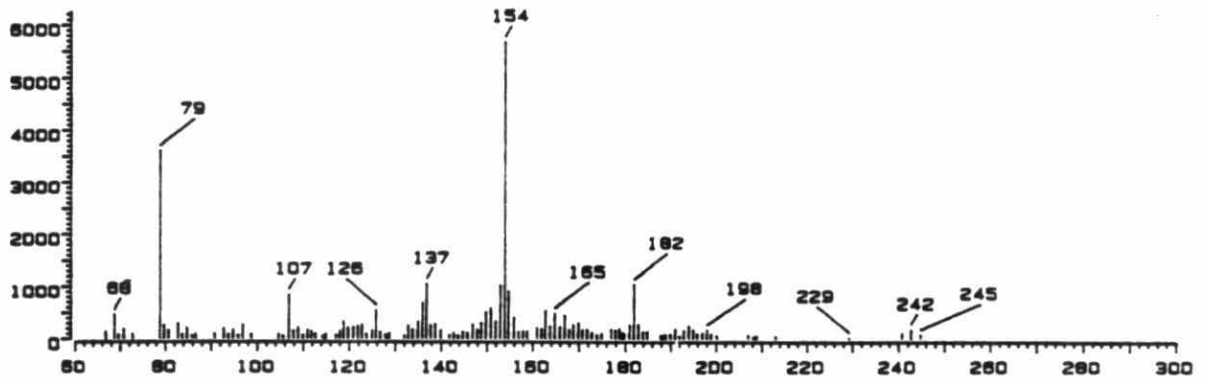


File >Y1745
8pk Ab 5681

LF-10-2

PCI

Scan 572
14.07 min.

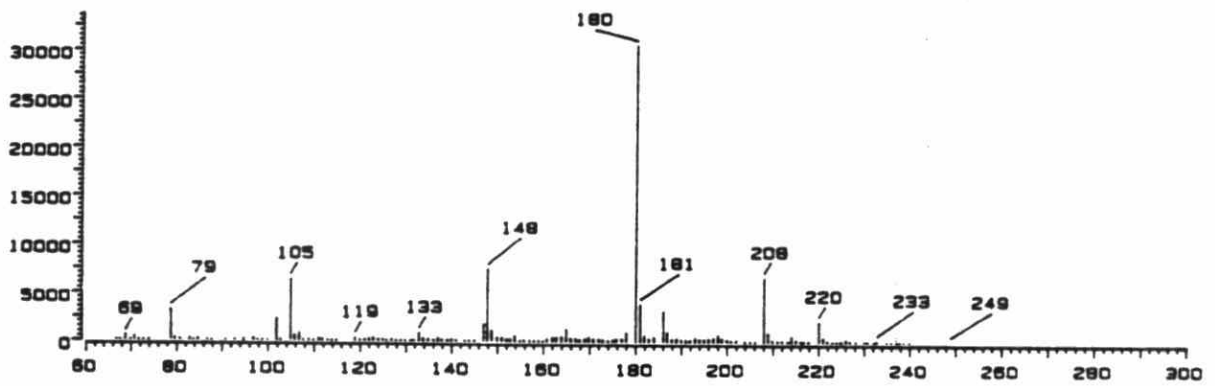


File >Y1745
8pk Ab 30584

LF-10-2

PCI

Scan 819
17.93 min.

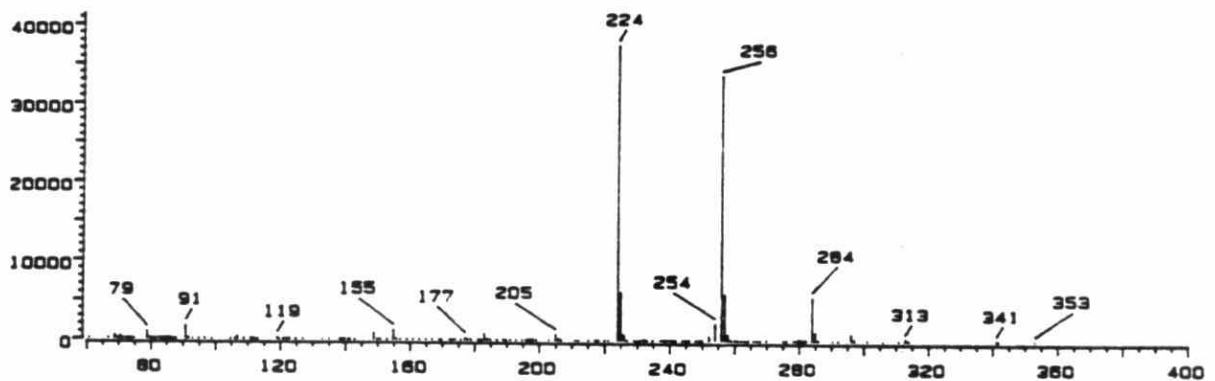


File >Y1745
8pk Ab 37600

LF-10-2

PCI

Scan 1787
32.74 min.

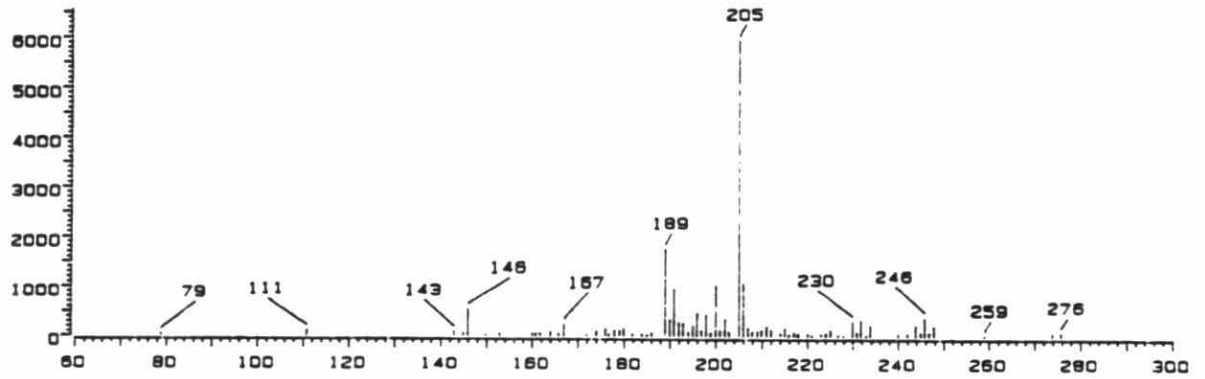


File >Y1500
8pk Ab 5959

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 987
20.78 min.

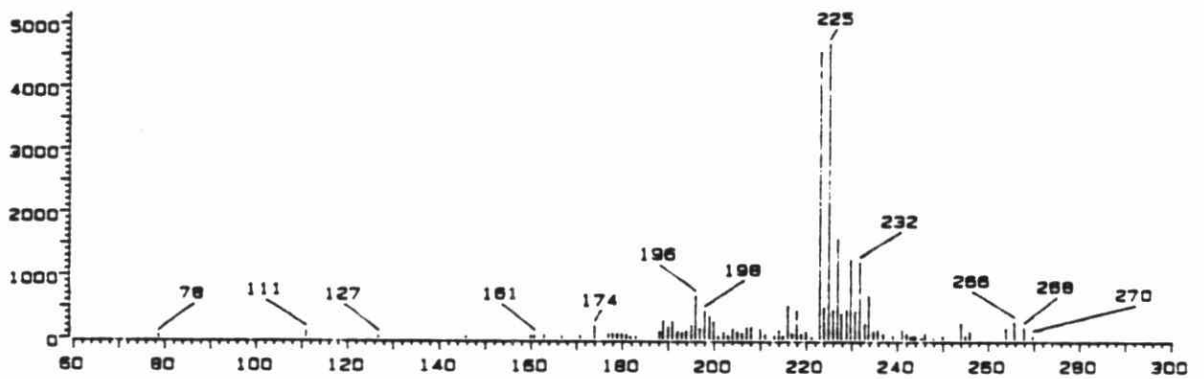


File >Y1500
8pk Ab 4692

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 1147
23.32 min.

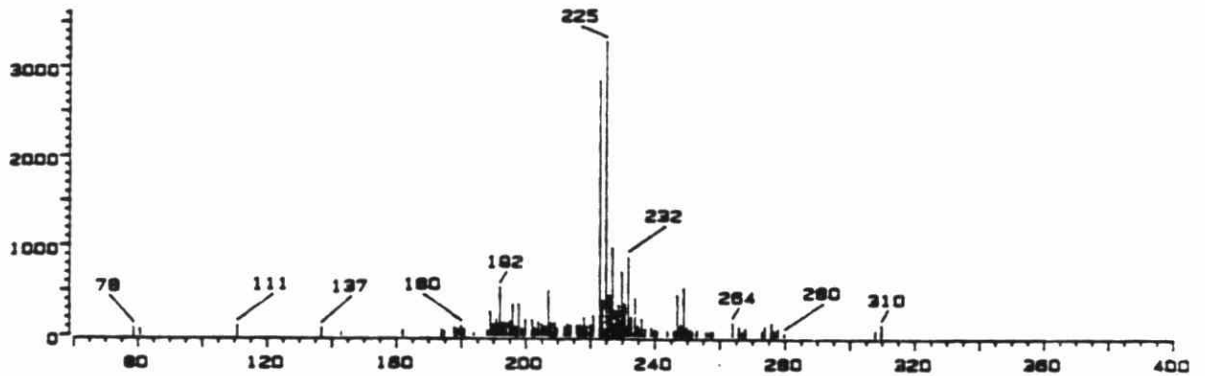


File >Y1500
8pk Ab 3287

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 1232
24.67 min.

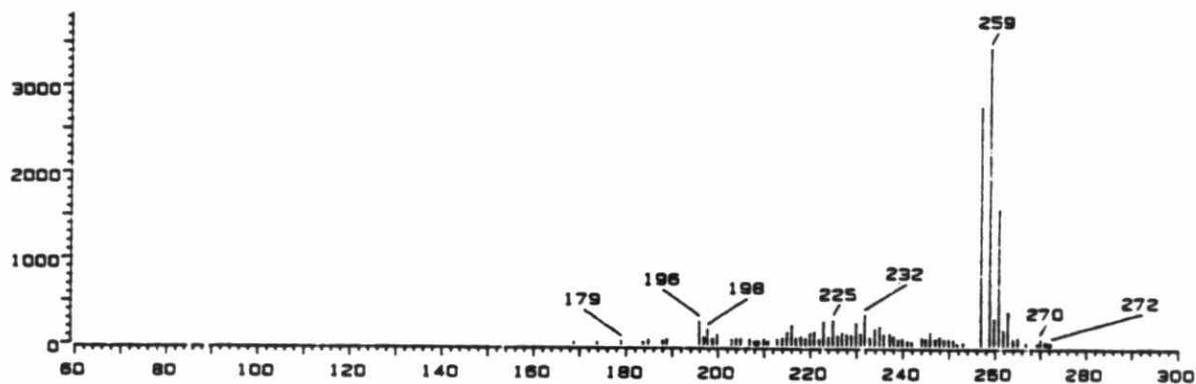


File >Y1500
Sph Ab 3482

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 1425
27.75 min.

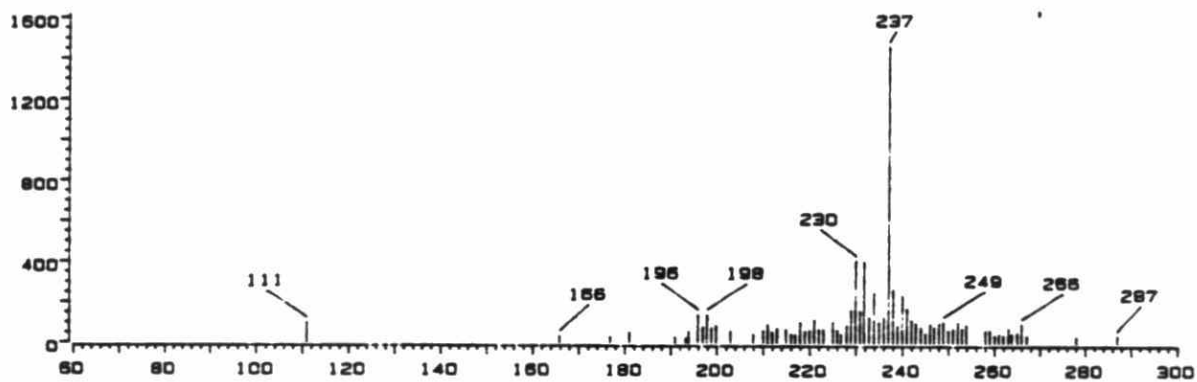


File >Y1500
Sph Ab 1468

LF-10-2-7

LF-10-2-7 (20uL) NCILIN

Scan 1529
29.40 min.



**TD
797
.K36
1987**

Leaching studies of
polychlorinated dibenzodioxins
and polychlorinated
dibenzofurans from municipal

76637